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CLAY-ORGANO STUDIES OF SELECTED CHERNOZEMS

by

MARVIN J. DUDAS, B.SC.



A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
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DEPARTMENT OF SOIL SCIENCE

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Clay-organo studies of selected chernozems" submitted by Marvin J. Dudas, B.Sc., in partial fulfilment of the requirements for the degree of Master of Science.

ABSTRACT

Black Chernozem soils occur in a wide belt through central and southern Alberta. The suggestion has been made that the Ah horizons of Black Chernozems located in the southern portion of the province have a "fluffy" microstructure whereas in northerly regions the Ah horizons seemed to have a stronger microstructure.

This study was undertaken to determine the differences, if any, in the mineralogy, chemistry, and structure of Black Chernozems located in the northern, central, and southern portions of the chernozemic belt and to determine the nature of clay-organo complexes.

For the investigation three major sampling areas were chosen and four profiles were sampled in each. Physical, chemical, mineralogical, and micropedological analyses were conducted in order to meet the needs of this study.

Analyses indicated that the polysaccharide and polyuronide content of Ah and B horizons from the southern area of the Black Chernozemic zone is higher than in samples from the central and northern areas. Humic acid extracted from Ah horizons from southern chernozems is of lower molecular weight and more aliphatic in nature. The microstructure of Ah horizons from the southern area consisted of tiny spherical plasmic granules

unassociated with mineral grains. The microstructure of Ah horizons from the northern and central areas was different in that there was intimate association of mineral grains with plasmic material and the granules were larger in size.

The mineralogy of C horizons for all profiles was found to be quite similar and characterized by a dominance of montmorillonite and illite. Kaolinite, chlorite, and interstratified clay minerals were also found in the C horizons. Analyses of the clay fraction from B horizons indicated that weathering of montmorillonite or organic interlayering occurs.

Evidence was obtained that a substantial amount of organic matter is complexed to clay minerals. In addition, it was found that the magnitude of clay-organo complexing is greatest in the fine clay fraction. Soils from the southern area exhibited the greatest degree of complex formation.

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I. INTRODUCTION

The classification of soils in the Black Soil Zone of Alberta has been to a large extent completed. Examination of the Soil Zone map for Alberta shows that the Black zone extends from 54° N latitude north of Edmonton to approximately 51° N latitude north of Calgary in a continuous band. There are, in addition, some large patches of Black soils extending almost to the United States-Canada boundary along the foothills of southwestern Alberta.

It is known that the climate and vegetation throughout this extensive area are somewhat different. During the mapping of these soils it was observed that there were morphological differences in the Orthic Black Chernozems between the northern and southern part of the zone. Even though both are classified the same, the Ah of the Orthic Black Chernozem in the southern part of the zone appears loose to soft granular whereas the Orthic soil in the northern region has a firm granular type of structure in the Ah horizon.

The purpose of this project is to determine whether or not differences exist among the Orthic Black Chernozems found in the northern, central, and southern portions of the described Chernozemic belt. To achieve this purpose it is felt that the following objectives should be pursued:

- (1) to compare the organic composition of the Ah and Bm horizons;

- (2) to compare the mineralogy of these soils;
- (3) to study organo-mineral complexes of these soils in a comparative vein.

II. LITERATURE REVIEW

Climate, Vegetation, and Geographical Distribution of Chernozem Soils

Chernozem soils are known to occur throughout the world in zones of similar climate and vegetation. The general features of the climate in the chernozem areas have been suggested by Dokuchaev (Joffe, 1949). They are: continentality, rainfall deficiency, low humidity, hot summers, cold winters, and sharp fluctuations in temperature. The rainfall deficiency is caused not so much by the low rainfall as by the character of fall and seasonal distribution. In the chernozem regions, the rain comes frequently in downpours, resulting in considerable runoff. The highest fall comes during the summer. Because of the high temperatures, low humidity, and high evaporation, less moisture is available for percolation and leaching.

The chernozem areas of the world are characterized by grass-land vegetation. Kubiena (1953) describes the plant cover of the chernozem region of Europe as grass steppe with Festuca, Stipa, and Koeleria species being predominant. In the moister parts of the grass landscape, on river banks, and in depressions, clumps of trees of the deciduous variety occur.

Within the USSR, the typical vegetation of the steppes' grassy flora are described by Klinka (1963) as associations of Stipa (S. pennata, S. capillata, S. stenophylin), Koeleria cristata, Festuca

sulcata, Poa bulbosa and Bromus inermis. In small hollows and at the head of ravines the so-called wet shrub vegetation consists of willow, poplar, and birch.

The Eurasian Steppes have been described by Keller (1927) as being similar to the true prairies of North America. In the Caspian and Central Asian area, he describes the vegetation as being composed predominantly by sod-forming grasses such as Stipa pennata, Festuca sulcata and Koeleria gracilis along with subordinate tussock grasses.

Common throughout the Great Plains area of the USA are mid-height grasses like Stipa comata, Agropyron sp., Koeleria cristata, Festuca sulcata with lower amounts of Bromus inermis (Eyre, 1963). Oak and poplar occur in moister regions such as draws and ravines.

Moss (1955) and Coupland (1961) regard the Festuca scrabella association as the climax vegetation of the Canadian parkland belt. In addition, Koeleria sp., Stipa sp., and Agropyron sp. are characteristic of the vegetation. Salix sp. and Populus sp. are commonly found in the moister areas.

Geographically, chernozem soils occur in four major world locations - United States, Canada, Europe and Asia, and Argentina.

In the United States, the chernozem soils occupy an area of 280,200 square miles (Joffe, 1949). The chernozem belt occupies approximately three-fourths of North Dakota, one half of South Dakota and Nebraska, three-fourths of Kansas, and one-half of

Oklahoma and Texas (Joffe, 1949). Smaller areas in the Columbia Plateau section of Washington, Oregon, and Idaho have also been recognized.

In Canada, the Black Chernozem soils occur in a thin belt starting in southwestern Alberta, extending northward to 54° N latitude, swinging eastward through central to southeastern Saskatchewan and including the southwest portion of Manitoba (Leggett, 1965).

According to the map of Glinka (Joffe, 1949), the chernozem soils of Europe extend in a belt running southwest to northeast through northern Bulgaria, Hungary, Rumania, and USSR. In the western part, it is found approximately at the 45° N latitude, and in the eastern part, at the 57° N latitude. In Asia, the chernozem belt is an extension of the European belt and terminates approximately at the 93° east longitude. A few scattered areas of chernozem and chernozem-like soils are found in northern China.

Papadakis (1963) has described chernozem-like soils in the pampas or grassland regions of Argentina. The area extends from Bahia Blanca northward to Cordoba, then east to Sante Fe and to the Atlantic Ocean.

Modal Concepts of Chernozem Soil

The term chernozem was first introduced by the peasants of Russia to describe the highly productive black soil they were farming. Literally, translated, the Russian word "chernozem" means black

earth. Usage of the term spread, resulting in a broadening of its original meaning. All pedologists have reserved the word "chernozem" for grassland soils in steppe regions, however, minor variations in climate and parent material throughout steppe regions of the world have resulted in somewhat different profiles being formed. Joffe (1949) and Klinka (1963) indicate that almost all of the chernozem soils in Europe have developed on highly calcareous loess material. In North America, the parent material on which chernozems have developed, is less calcareous. In addition, these authors point out that the rainfall in the grassland regions of Argentina and North America is somewhat higher than for the comparable regions in Europe.

Modal profiles and their features. In Russia several varieties of chernozem soils have been singled out. The basis for separation appears to be differences in the thickness of humus horizons, content of humus, as well as morphological peculiarities which are reflections of slight climatic differences. Klinka (1963) from a review of the Russian literature presents the following group of chernozem soils recognized by Russian pedologists. They are:

1. Thick Chernozem
2. Ordinary Chernozem
3. Southern Chernozem
4. Azov Chernozem
5. Leached Chernozem

The Thick Chernozem is depicted by Russian scholars as the modal chernozem soil. It is centrally located in the described chernozem area; the other varieties appear in locations deviating from the central area. As described by Klinka, the Thick Chernozem is characterized by a humus horizon which varies from 100 to 120 cm in depth. The A horizon is homogeneous having a dark, almost black color with a distinct granular structure. The bottom of the A horizon in some cases becomes granular-lumpy to lumpy in structure. Effervescence starts either in the lower portion of the A horizon or immediately underneath.

Ordinary Chernozems differ from the Thick Chernozem in that the depth of the humus horizon is generally 65 to 80 cm in depth. In addition, the A horizon is more gray in color than the thick variety. The structure has been described as lumpy-granular becoming lumpy in the lower part of the A horizon. Carbonates are present immediately beneath the A horizon and at times infuse the lower part of the humus horizon.

The Southern Chernozems formed in the drier steppe regions have much thinner A horizons. Nikiforov (Glinka, 1963) describes the Southern Chernozems as having a humus horizon of thickness 30 to 40 cm. The upper A horizon is light gray in color having vertical cracks which divide it into coarse, block-like clods. The lower A horizon has a more brownish color being more or less compacted. Below the A horizon occurs a B horizon which lacks

humus, and has a definite prismatic structure. Nikiforov indicates that the walls of the prisms are shiny and have a darker color than the material within the prisms. Calcium carbonate accumulation occurs at a depth of 60 to 90 cm from the surface.

The Azov Chernozem stands out by the great thickness of its humus horizon which in places amounts to a depth of 140 cm. The color of the humus horizon is not as dark as the thick variety having grayish-black or brownish tinges. The structure is nut-like, loose and friable.

The Leached Chernozems have a humus horizon 90 to 100 cm thick. The top part of this horizon is granular but becomes granular-lumpy lower down. The distinct feature of this soil is the presence of a brown colored B horizon which is free, or almost free of calcium carbonate. Beneath the B horizon there occurs a horizon considerably enriched by CaCO_3 .

In Europe, Kubiena (1953) has classified Chernozems under Steppe Soils. In the classification of soils, Kubiena has placed considerable emphasis on humus forms. Of the terrestrial humus forms, the mull type is characteristic of chernozem soils. Much of the morphology and genesis of chernozems is inherent in the description of mull humus. According to Kubiena, mull humus is formed in areas with mild to warm soil climate; the soils are sufficiently high in clay and nutrients with balanced water conditions and aeration. The plant cover is of the type which yields easily

decomposable plant remains of high biological value. Externally, mull humus soils appear gray, brownish gray, dark gray to black in color giving a crumbling plastic mineral soil colored by diffuse humus substances. Microscopic investigations show that recognizable cell structures of plant and animal remains are missing and no large humus particles are present. Humus substances and clay cannot be separated at all mechanically and only inadequately by chemical methods giving rise to new bodies called clay-humus complexes which are characteristic of true mull formation.

Two types of chernozem soils are presented by Kubiena - the Typical Chernozems and the Degraded Chernozems. The Typical Chernozem is described as a moderately calcareous soil having a dark-gray, brownish-gray or black A horizon characterized by an excellent mull humus. The depth of the humus horizon may be up to one meter or more. The structure of this horizon is stable crumb-like with a spongy microfabric. The A horizon is immediately underlain by a carbonated C horizon. The chemical characteristic is the high amount of calcium present. In the normal Degraded Chernozem, the A horizon is shallower than the typical variety. A diagnostic feature of the degraded type is the presence of a brown colored B horizon. Both A and B horizons are free of chalk. An excellent mull type of humus forms in the surface horizon. A strongly developed Ca horizon occurs below the B.

In Canada, the modal concept of orthic Black Chernozem soils

has been defined by the National Soil Survey Committee (1965) as being the well-drained member of the Black Great Soil Group. By definition, orthic Black Chernozems have an Ah horizon of sufficient thickness to produce an Ap horizon of at least 6 inches in thickness and having dry Munsell color values less than 4.0 and chromas less than 2.0 dry. This "A" horizon is underlain by a color Bm horizon which is free of carbonates, or by a weakly textural Btj horizon. A lighter colored horizon of carbonate concentration is usually present but it is not an essential criterion. According to Joffe (1949), chernozemic soils in North America are characterized by the high organic matter content and granular structure of the A horizon. The B horizon is usually prismatic in macrostructure, breaking to blocky or coarse granular aggregates, the latter tendency increasing with clay content.

In the United States, the modal concept of chernozem soils is similar to that held in Canada for Orthic Black Chernozems. Marbut (Joffe, 1949) indicates that the A horizon of chernozem soils in the United States does not attain a thickness of more than 20 inches. McClelland et al. (1959) describes the chernozems of eastern North Dakota as having black, granular A horizons that are 5 to 14 inches in thickness with a pH ranging from 6.5 to 7.5. The B horizon is usually a color B but it may be a textural B with clay films on ped faces. Structurally, the B horizon is usually prismatic, breaking to blocky; its pH ranges from 6.5 to 8.0 or greater if lime occurs in

the lower portion of the horizon. The thickness of the B horizon is usually the same as that of the A horizon.

A correlation of the terminology used in various countries for description of chernozem soils is presented in the following table.

Process of Soil Formation

Dokuchaev initially proposed that the soil is a result of the combined activity and influence of parent material, vegetation, climate, topography and time. These influences have been termed the soil forming factors.

The dominant soil forming process in the development of chernozem soils is referred to as calcification. According to Lutz and Chandler (1946), calcification is the process of soil formation in which the soil is kept supplied with sufficient calcium to maintain the colloids in a high state of base saturation.

The universal characteristic of chernozems recognized by all pedologists is the type and amount of organic material which has accumulated in these soils. The role of calcium in the formation of chernozem soils is manifested in its effect on organic matter accumulation. Gedroiz (Joffe, 1949) explains the relation of calcium to chernozem formation emphasizing the role of calcium in stabilizing organic materials. In Gedroiz's words, "the decomposition of organic remains in a normal chernozem takes place in a medium sufficiently rich in calcium to saturate the absorption capacity of organic matter, thereby fixing it and lowering its solubility and

Comparative Classification of Chernozems

Country:	Russia	Canada	Europe	Argentina	United States
Source:	Glinka (1963) Joffe (1949)	National Soil Survey Committee (1965)	Kubiena (1953)	Papadakis (1964)	7th Approximation Smith (1965)
Profile type:	A-C profile - Calcareous parent material				
Approx. equivalents	Ordinary Chernozem	Rego Black	Typical	Calcareous	Entic Haploborolls
	Thick Chernozem	Chernozem	Chernozem	Chernozem	Haplic Calciborolls
Approx. equivalents	Azov Chernozem	Calcareous Black			Calcic Cryoborolls
	(Southern Chernozem)	Chernozem			
A-B-C profile - Calcareous parent material					
Approx. equivalents	Southern Chernozem	Orthic Black	Degraded	Parachernozem	Typic Cryoborolls
	Leached Chernozem	Chernozem	Chernozem		Typic Haploborolls
					Typic Argiborolls

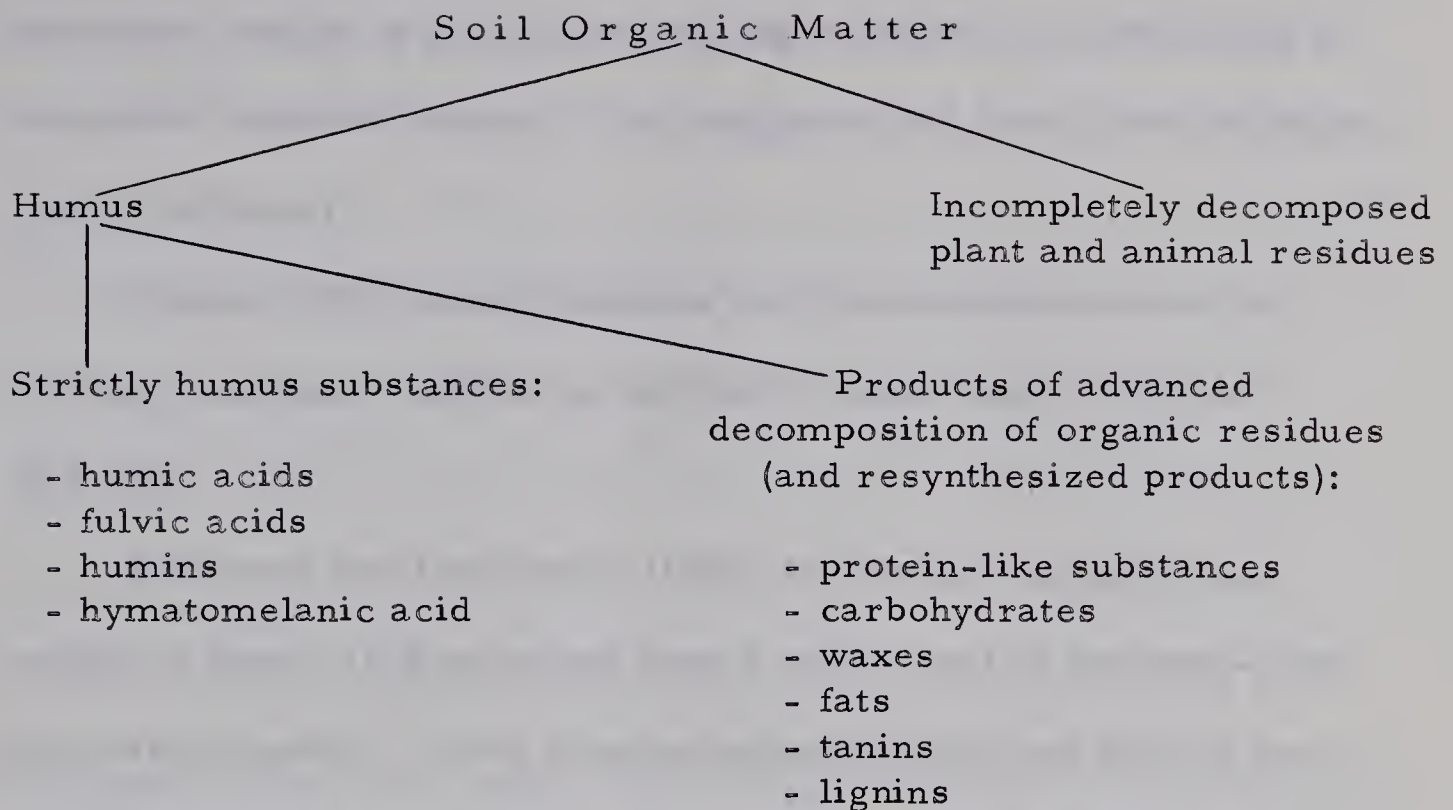
degree of dispersion. Mineralization of the organic matter is interrupted at an early stage and, because of its saturation with calcium, it attains a large grained, stable microstructure, becomes stable towards water, and colloiddally dissolves but little. The soil microorganisms find little organic matter at their disposal, even though all other conditions might be favorable for their activities. The organic substances, non-nitrogenous and nitrogenous, are only slightly mobile notwithstanding the large quantities present in the soil."

A consideration of the climate in the chernozem regions indicates that grass vegetation is highly favored (Moss, 1955). Grasses, because of their dense rooting system, contribute large amounts of organic material to the soil most of which is deposited in the soil. Under mixed steppe vegetation, Kononova (1966) reports that from 65 to 90 per cent of the total plant mass dies annually, equivalent to 10 tons per hectare or more. According to Buchman and Brady (1961), grasses are particularly effective in returning bases to the surface of the soil, and as a result of their extensive root system, they also supply large amounts of organic matter. The combined effects of climate, vegetation, and calcium explain the salient features of chernozems - the presence of an organic-mineral horizon high in humus which is stable to degradation and translocation.

Soil Organic Matter

Organic matter and humus. In the literature one frequently encounters the terms "soil organic matter" and "humus" used interchangeably. There is, however, a basic difference between these two terms. Soil organic matter consists of any substance of organic origin, living or dead, occurring in the soil. That portion of the organic matter which has undergone decomposition to such an extent that one can no longer determine the nature of the material from which it was derived is termed humus (Joffe 1949, Kubiena 1953).

More contemporary ideas on the composition of soil organic matter have resulted in the classification of the whole diversity of soil organic compounds into two main groups. Kononova (1966) presents the first of these groups as the compounds of non-specific nature which includes the fats, carbohydrates, proteins and their decomposition products, lignins, tannic substances, and resins. The second group, because they cannot be related to existing groups of organic chemicals, is singled out as humus substances. Kononova reports that of the total reserve of organic matter, up to 85-90 per cent consists of humus substances. The scheme proposed by Kononova subdivides soil organic matter as follows:



Important Soil Organic Fractions

Humic acids.

Composition - By alkali fusion, Shmuk (Kononova, 1966) showed the presence of the aromatic ring in humic acid from chernozem soil. Among the fusion products he found were indole, derivatives of pyrrole, and derivatives of polyphenols and protocatechuic acid. Shmuk attributed their presence in humic acid to lignin and tannic substances.

Size and shape - Stevenson, et al. (1953) extracted humic acid from a soil located in the Ohio State University Farm with neutral sodium pyrophosphate. Using ultracentrifugation, electrophoresis, and diffusion experiments the authors concluded that the average

molecular weight of the colloid was approximately 53,000 having a somewhat spherical shape. They suggested the humic acid molecule may be solvated.

Posner (1963) using Sephadex gel filtration determined the average molecular weights of soil humic acids to be 70,000 to 200,000.

Schnitzer and Desjardins (1962) determined the molecular weight of humic acid extracted from a podzol soil by freezing-point depression method. They obtained values of 1684 and 669 for the A₀ and Bh horizons respectively. From the molecular weights, in conjunction with ultimate and functional group analysis, the molecular formulas were calculated as C₇₅H₃₃O₁₇N₃(COOH)₃(OH)₁₂(CO)₂ for the A₀ humic acid and C₂₁H₁₂(COOH)₆(OH)₅(CO)₂ for the Bh humic acid.

Wright et al. (1958) found the average molecular weight of humic acid to range from 47,000 to 53,800 as determined by osmometry. Other workers (Greenland, 1965) have reported values in the range of 20,000 to 50,000 with some investigators suggesting molecular weights over 100,000.

Visser (1963) studied humic acid extracted from a tropical sphagnum deposit with the electron microscope. In his electron micrographs, the humic acid sample appears to be condensed into small aggregates with an average size of approximately 80 Å. Flaig, Beutelspacher, and Kukharensko (Kononova, 1966) concluded from

their electron microscopic investigations that humic acids consist of tiny particles capable of uniting into chains and of forming racemose aggregates. These authors are of the opinion that humic acids consist of sphero-colloids aggregated into a loose, spongy structure. X-ray diffraction studies of humic acid by Sawyer (1962), Visser (1963), Kononova (1966) and others indicate humic acids are amorphous in structure.

Functional groups - Almost all possible groups such as carboxyls; phenolic, enolic, and alcoholic hydroxyls; quinones; esters; and ethers have been mentioned as group constituents of humic acid but there is no agreement as to their amounts or even on their very existence. (Dubach et al., 1963). Because of the peculiar nature of humic acid, the methods for extraction, and the lack of adequate criteria for their purity, contradictory results have been obtained even with comparable humic acid preparations. Of the possible mentioned functional groups, Bremner (1956) is of the opinion that the carboxyl and acidic hydroxyl groups play the most significant role in humic acid properties. It is these groups which are chiefly responsible for the exchange capacity of humic acids.

Wagner (1965) analyzed humic acid from a brunizem soil by a combination of chemical and infrared techniques. Of the total exchange-absorption capacity for the humic acid, 390 meg/100 g was attributed to carboxyl groups, 390 meg/100 g was attributed to

total hydroxyl groups where two-thirds of the total OH groups was phenolic in nature. Kononova (1966) reports values for the exchange-absorption capacity of humic acid separated from Chernozem soils, Podzolic soils, and Dark Chestnut soils as 474, 345, and 483 me./100 g respectively. The importance of the high exchange-absorption capacity for organic material has been demonstrated by Broadbent's (1955) study. He examined five soils containing from 5 to 10 per cent organic matter. The organic exchange capacities were obtained from samples treated with hydrochloric-hydrofluoric acid mixture to destroy the clay. The inorganic exchange capacities were obtained from samples treated with hydrogen peroxide to destroy the organic matter. He found that the organic fraction was responsible for 58 to 83 per cent of the sum of the exchange capacities of the two fractions.

Fulvic acids. These are a more heterogeneous group of humus material. Fractionation by chromatographic methods (Forsyth, 1947) have shown that the principal components are a group of phenolic materials similar to humic acids. According to Kononova (1966), fulvic acids are of lower molecular weight than humic acids and contain groups of polysaccharides. Barker (1964) using Sephadex fractionation, isolated 30 per cent of the fulvic acid carbon as polysaccharide materials. The high viscosities of fulvic acid solutions indicate that they are large, linear and flexible molecules. Uronic groups are usually present with the polysaccharides but the

proportion of carboxyl groups is much less than with humic acids (Greenland, 1965).

Polysaccharides. Polysaccharides are considered by Kononova (1966) as products formed from microbial activity. Forsyth (1950) found that polysaccharides extracted from diverse types of soils yielded essentially the same sugars on hydrolysis which suggested to him that polysaccharides were complex synthetic microbial products. Among the sugars identified by Forsyth were: galactose, galacturonic acid, glucose, mannose, arabinose and xylose. Parsons and Tinsly (1961) obtained the mannose, rhamnose and hexosamines from polysaccharide material in soils. They stated that soil polysaccharides are microbial in origin, since these sugars are not normally found in plants. Gupta et al. (1963) extracted the hydrolyzable portion of the organic matter from a variety of soils and analyzed for sugar content. In general, glucose was found to be dominant in all horizons of several soils (podzol, gray wooded, dark brown solodized solonetz, orthic black chernozem). Other sugars were found to occur in the extracts in the following decreasing order of abundance: galactose, mannose, arabinose, xylose, rhamnose, and ribose. Similar results are reported by several authors (Salmon, 1963; Dorman, 1967; Johnston, 1961; Gupta and Sowden, 1963).

Polyuronides are mainly glucuronic and galacturonic acids. These uronic acids may be described as sugar acids containing aldehyde and carboxylic groups. They differ from the other hexoses in that the anhydroxyl group is replaced by the carbonyl group.

Graveland (1961) has shown these acids to exist in the soil but in lower concentrations than the true sugars.

Role of Organic Matter in the Formation of Soil

In considering the important effects of organic matter on soil formation, it should first be mentioned that soil formation is closely linked with the action of diverse forms of organic substances on the parent material. This has been labelled as the bio-geochemical process. The importance of organic matter in soil is implicit in the definition of soil which recognizes fertility as a unique and constant feature distinguishing soil from the parent rock. In the formation of a fertile soil, organic substances play a direct role since they are the sources of plant nutrients which are liberated in available forms during mineralization. But organic substances also play an indirect role. The supplies of nutrients and water for the plant are most readily provided in soil of good structure; in building soil of good structure organic substances represent the most important factor.

The heterogeneity of a soil results from the alteration of the parent material and the redistribution of materials during the soil-forming process. In this process, soil organic matter plays an important role. The degradation, translocation and redistribution of inorganic constituents as influenced by organic materials have been studied by numerous investigators.

Aleksandrova (1954) and Kononova (1966) suggested that

sesquioxides may be complexed with humic acids or humates. Yarkov (1956) attributed the sesquioxide complex to fulvic and other lower molecular weight acids. Wright and Schnitzer (1963) suggest that fulvic acid initially forms a water-soluble multidentate chelate with metals such as iron and aluminum. Precipitation of these metal-organic complexes occur when the downward leached complex reacts with ionic Ca^{++} and/or Mg^{++} . According to Pawluk (1960), the depth of Ae development in Gray Wooded soils is dependent upon the depth of penetration of the organic acids. The penetrating acids, if in the hydrogen form, exchange for aluminum and other stabilizing ions on the clay complex. The exchange for hydrogen may have a partial dispersing effect on the clay particles as well as a dissolution effect. This would result in a mild weathering of the clay minerals. Duchaufour (1960) is of the opinion that water soluble organic materials favor and maintain dispersion of the clay and thus are one of the main factors in "lessivage". Schnitzer and Delong (1955) state that aqueous extracts of many vegetation materials have the ability to reduce iron. Bloomfield (1957) further suggests that the reduction and solution of ferric oxides can be attributed to the action of carboxylic acids and polyphenols.

Numerous investigations of such nature all suggest some intimate type of interaction between the organic and inorganic soil fractions. The exact nature of these interactions are at present not fully clear.

Tyurin (Kononova, 1966) has classified the possible forms of link between humus substances and the mineral part of the soil. His classification may be represented as follows:

1. Humus substances occurring in a free or almost free state.
2. Humus substances in the form of strong base humates.
3. Humus substances in the form of humates and gels mixed with aluminum and iron hydroxides.
4. Humus substances firmly linked with clay.
5. Humus substances in the form of complex organo-mineral compounds (with Al, Fe, P, S).

In view of the many studies presented in the literature, this classification seems to be too general. Humus has been defined as a group of organic matter composed of several empirically defined fractions (humic acids, fulvic acids, etc). Several of these fractions have been singled out as somewhat sole participants in certain organic-inorganic soil reactions. A more specific classification is presented by Antipov-Karataev (1966) in which the recognized classes of metallo-organic compounds are:

1. Salts of low-molecular-weight organic acids.
2. Salts of humic and fulvic acids.
3. Complex and intra-complex compounds (chelates).
4. Adsorption organo-mineral compounds which include compounds of fulvic and humic acids with hydrated

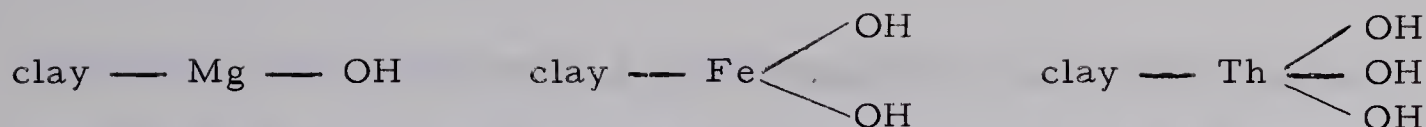
sesquioxide and adsorption compounds with clay particles.

Organo-Mineral Compounds in Chernozems

Considering the climatic features and high base saturation status of chernozem soils, many of the degradation and translocation processes which have been shown to occur in podzolic soils (Bloomfield, 1965) are not operative in chernozems. The high accumulation of organic matter in the A horizon coupled with minimal development of a B horizon is indicative of relatively stable organic and inorganic soil constituents in chernozem soils. The salient feature of organic substances in chernozem soils is their existence as organo-mineral complexes (Kubiena, 1963).

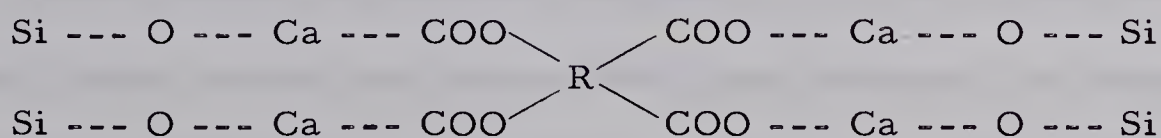
Possible Mechanisms and Site Locations of Complexing

One of the first suggestions of a possible mechanism of complexing between mineral and organic compounds came from Bower and Truog (Peterson, 1947). Results of their study showed that where polyvalent cations were used to saturate clays, higher saturations were obtained than when monovalent cations were used. Furthermore, the authors noted that the results with monovalent cations were in good agreement where as those with polyvalent cations were increasingly higher with decrease in the strength of the base formed by the respective cations. Diagrammatically, the authors pictured adsorption of polyvalent cations as:



According to this diagram, not all the charges of the polyvalent cations are used by a single clay. The surplus charges are available for attracting to the cation some other negative ion such as hydroxyl groups as shown, other clay particles, or organic ions.

Gapon (Peterson, 1947) has proposed a somewhat similar idea for calcium linkage between the oxygen layers of silica sheets and negative humic acid particles. He shows the bridging by the following diagram:



Similar types of linkage could occur for other polyvalent cations.

Quantitative studies by Evans and Russell (1959) and Martin and Reeve (1960) with humic acids have shown that there is no adsorption by sodium saturated montmorillonite. This tends to support Gapon's and Truog's postulate that residual positive charges of divalent and trivalent cations are available for attracting anionic species.

Kohl and Taylor (1961) studied the nature of complex formation between H and Ca bentonites and organic compounds containing the carbonyl group. Infrared analysis showed that hydrogen bonding between the double-bonded oxygen of the carbonyl group and the clay mineral occurred. X-ray diffraction studies revealed no expansion

of the lattice took place leading to the suggestion that hydroxyl groups exposed on the broken edge of the clay crystal could be the reactive site. Larson and Sherman (1964) extended Kohl and Taylor's IR study to the examination of clay — OH groups as the source of carbonyl hydrogen bonding. In most cases the authors found that clay — OH absorption bands shifted to longer wave lengths indicating a weakening of the hydroxyl stretching. This suggested that clay hydroxyl groups as participants in the reaction with carbonyl group containing compounds.

Recent studies by Aleksandrova and Nad (1958), Evans and Russell (1959), Martin and Reeve (1960), and Schnitzer and Skinner (1964) have shown that humic and fulvic acids are readily adsorbed by freshly synthesized iron and aluminum oxides. Aleksandrova et al. (1958) noted that old, crystalline forms of the oxides are less reactive than freshly precipitated material. These observations support the suggestion that aluminum and iron oxides may act as bridges linking humic and fulvic acids to clay lattices. The exact manner in which the humic materials are complexed to clays through iron and aluminum is not established; ionic interaction, coordination or chelation or all three could be involved (Greenland, 1965). X-ray studies by Evans et al. (1959) have shown that humic acids do not penetrate the interlamellar region of clay minerals.

No extensive studies of the adsorption of polysaccharide materials separated from soils have yet been reported. Greenland (1956) has

shown that a wide variety of sugars formed interlamellar complexes with montmorillonite. In addition, polysaccharide isolated from the soil was shown to cause lattice expansion.

Kubiena (1953) considers that the processes involved in the formation of clay - humus aggregates in soils are only fully seen when soils are studied with the light microscope. The use of micropedological techniques has recently received considerable attention however many of the investigations are related to clay movement, cutan formation, and mineral weathering. Greenland (1965) states that the processes involved in complex formation between organic and inorganic soil constituents take place at the molecular level and the light microscope can not provide information about such processes. The fact not pointed out by Greenland is that organo-mineral complexes may express their features in soil aggregation and structure which can be studied by thin section analysis.

Summary of Literature Review

Chernozem soils have been shown to occur regionally throughout the world in zones of similar climate and vegetation, although Russian pedologists have recognized a variety of local chernozem soils associated with slight climatic variations within the general climatic features of the steppe soil regions.

The most outstanding feature of chernozem soils has been expressed to be the high accumulation and stability of organic matter. Several workers have progressed in characterizing the forms of organic matter in chernozem soils with major emphasis placed on the humic acid, fulvic acid and polysaccharide fractions. Combined results of various investigators indicate that humic acids are basically phenolic compounds combined in a manner as yet unknown to form a group of high-molecular-weight-polymers. Studies on humic acid indicate relatively high exchange-absorption capacity principally due to carboxyl and hydroxyl groups. Fulvic acids have been suggested as being similar in composition to humic acids but of lower molecular weight. Important polysaccharides in soils appear to be the simple sugars and uronic acids. The polysaccharide content of organic matter is significantly lower than the humic acid content.

The stability of organic matter in chernozem soils has been regarded by soil scientists as the result of the formation of organo-mineral complexes. The exact details of complex formation is still

in doubt. Empirical studies have shown that iron and aluminum play an important role in the formation or union of organic and mineral compounds. Infrared studies indicate importance should be attached to the role of carboxyl, phenolic hydroxyl and alcoholic hydroxyl groups in complex formation. The role of calcium in stabilizing organic material is well recognized; suggestions have been made that linkages between exposed clay hydroxyl groups and organic anionic groups occur through calcium bonding.

In conclusion, chernozem soils throughout the world have received considerable attention most of which in recent years has been directed to the organo-mineral complexes occurring in these soils. Although some progress has been made concerning organo-mineral complexes, many problems still remain unsolved as far as mechanisms of complexing and fractions involved.

III. MATERIALS AND METHODS

Materials

The three sampling areas in the Black Chernozem area of Alberta used for this study are shown in figures 1, 2 and 3. Within each area four sites were chosen and one profile at each site was sampled. All sites were chosen on well-drained undulating topography. Most sites had a southern or southeastern aspect. Typical profile descriptions are given in tables I to III for one profile from each of the three major sampling areas.

The climate in all three areas is subhumid with a mean annual precipitation of 16 to 18 inches and a mean annual daily temperature of 36° F to 40° F. The Pincher Creek area has the highest values for precipitation and temperature. In addition, the wind velocity in the Pincher Creek area during the growing season is 11 to 12 miles per hour whereas the value for the Olds and Edmonton areas are seven to eight miles per hour.

Generally, the native vegetation consists of a variety of grasses as well as poplar and willow. The dominant grasses found in the three sampling areas were:

- (1) Festuca sp.
- (2) Stipa sp.
- (3) Koeleria cristata
- (4) Poa sp.

(5) Bromus inermis

(6) Phleum sp.

Other plants found in the sampling areas were rose, lupine, vetch and cinquefoil.

The lack of strictly virgin sites in the Olds and Edmonton areas made it difficult to compare vegetation as closely as was desired. In general, the basic vegetative difference was observed in the trees and shrubs of the areas concerned. In the moister regions of the Pincher Creek area there was a predominance of Salix sp. where as similar sites in the Edmonton and Olds areas consisted of Populus tremuloides with lesser amounts of Populus balsamifera and Salix sp. Although Populus sp. was noted in the Pincher Creek area, it was much smaller in size.

The parent material of the three areas is calcareous till. In the Pincher Creek area the underlying strata comprise the Belly River Formation characterized by gray and green sandstone and shale; bentonites, carbonaceous and concretionary shales, conglomerate and coal. Till in the Olds area is underlain by the Paskapoo Formation consisting of sandstone, shale, conglomerate, bentonitic shales, siliceous limestone and thin coal beds. In the Edmonton area, the Edmonton Formation is the underlying strata which consists of gray bentonitic sandstone and shale; gray, greenish and carbonaceous shale, conglomerate, bentonite and coal.



Figure 1 Map showing sampling sites in the Edmonton area.



Figure 2 Map showing sampling sites in the Olds area.

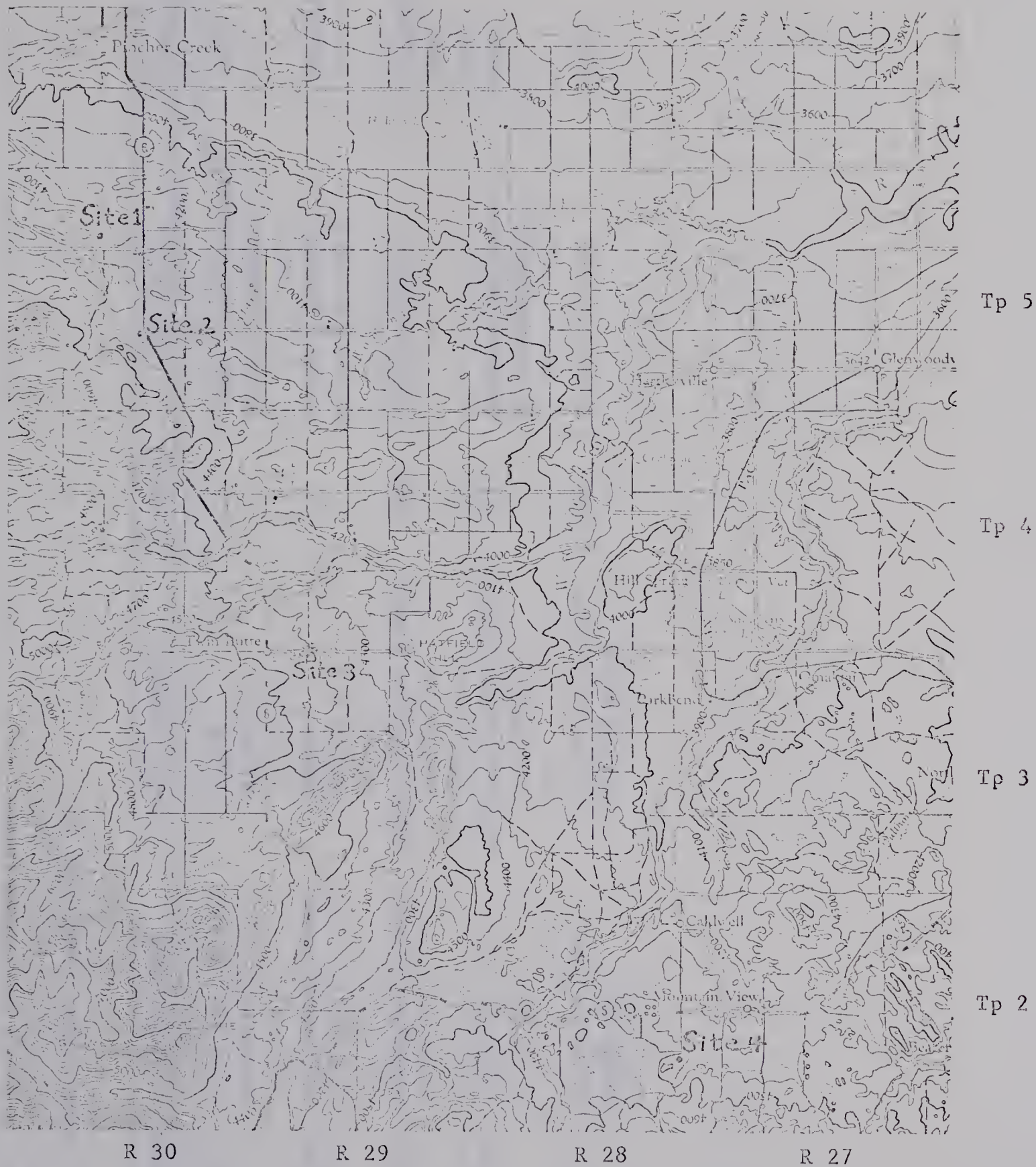


Figure 3 Map showing sampling sites in the Pincher Creek area.

TABLE I. Profile Description of Site 3 - Edmonton Area

Location: NE 19-48-21 W4

Classification: Orthic Black Chernozem

Series Name: Beaverhills Loam (Bh. L)

Horizon	Depth	Color Dry	Color Moist	Texture	Structure	Consistence
Ah ₁	0-6"	very dark brown 10 YR 2/2	black 10 YR 2/1	L	very weak prismatic to fine granular	soft
Ah ₂	6-16"	very dark brown 10 YR 2/2	black 10 YR 2/1	L	weak prismatic to medium SAB	friable
Btj-Bm	16-23"	yellowish brown 10YR 5/4	dark yellowish brown 10YR 4/4	HvL	medium SAB	slightly firm
BC	23-30"	brown 10 YR 5/3	dark yellowish brown 10 YR 4/4	CL	medium prismatic to coarse blocky	firm
C _k	+30"	grayish brown 10 YR 5/2	yellowish brown 10 YR 5/4	CL	pseudo-blocky	firm

TABLE II. Profile Description of Site 1 - Olds Area

Location: SW6-34-1 W4

Classification: Orthic Black Chernozem

Series Name: Antler Loam (Ant. L)

Horizon	Depth	Color Dry	Color Moist	Texture	Structure	Consistence
Ah ₁	0-5"	black 10 YR 2/1	black 10 YR 2/1	L	weak prismatic to fine granular	soft
Ah ₂	5-16"	very dark brown 10 YR 2/2	black 10 YR 2/1	L	coarse prismatic to weak fine-med- ium granular	friable to slightly firm
Bm	16-23"	brown 10 YR 5/3	dark yellowish brown 10 YR 4/4	Hv, L	strong coarse prismatic to medium SAB	slightly firm to firm
C _{ca}	+23"	light brownish gray 10 YR 6/2	brown 10 YR 5/3	HvL-CL	massive	-

TABLE III. Profile Description of Site 1 - Pincher Creek Area

Location: SE 27-5-30 W4

Classification: Orthic Black Chernozem

Series Name: Dunvargen Loam (Dv. L)

Horizon	Depth	Color Dry	Color Moist	Texture	Structure	Consistence
Ah ₁	0-4"	very dark brown 10 YR 2/2	black 10 YR 2/1	L	fine granular	soft
Ah ₂	4-10"	dark grayish brown 10 YR 3/2	black 10 YR 2/1	L	fine granular	slightly hard
Bt _j	10-16"	dark brown 10 YR 3/3	dark brown 10 YR 3/3	Hv. L	weak coarse prismatic to strong med- ium SAB	slightly hard
Bc	16-29"	brown 10 YR 5/3	dark brown-brown 10 YR 3/3 - 4/3	CL	weak coarse prismatic to mod. fine SAB	friable
Cca	29-39"	light gray 10 YR 7/1	grayish brown 2.5 Y 5/2	CL	pseudo-angu- lar blocky	very friable
Ck	+39"	-	grayish brown 2.5 Y 5/2	CL	pseudo-angu- lar blocky	very friable

Methods

The collected samples were oven dried at 60° C for 12 hours. They were then ground in a steel-roller mill to pass a 2 mm sieve and stored in non-sealing screw top containers.

1. Routine analyses.

(a) Mechanical analyses - The pipette method described by Toogood and Peters (1953) was used for mechanical analysis. Salts were removed from the soil with repeated washing; organic matter with H₂O₂; and calcium carbonate with the addition of 0.1 N HCl. Fine clay content was determined by evaporating an aliquot separated from the total clay fraction by centrifugation as outlined by Baver (1959).

(b) Hygroscopic moisture - Hygroscopic moisture was determined by oven drying samples overnight at 105° C.

(c) Soil reaction - pH values were determined on a saturated soil paste as outlined by Doughty (1941) using a Beckman model zeromatic pH meter equipped with a glass and a calomel electrode.

(d) Total carbon - A Leco, model 577-100 carbon analyzer was used for the determination of total carbon. The samples were ground to pass a 60-mesh sieve before being placed in the induction furnace.

(e) Total nitrogen - The Kjeldahl-Wilfarth-Gunning method (A. O. A. C. 1955) was used for the determination of total nitrogen. The catalyst used was HgO (0.41 g), CuSO₄ (0.08 g) and K₂SO₄ (9.9 g) packaged in a polyethylene bag and sold commercially as Kel-pak. The ammonia was collected in a 4% H₃BO₄ solution as suggested by Meeker and Wagner (1933) and titrated against standardized H₂SO₄.

(f) Calcium carbonate equivalent - A modification of the procedure described in A. O. A. C. (1955) was used to determine carbonate carbon. The CO₂ evolved by treating the sample with H₂SO₄ and FeSO₄ was absorbed in ascarite and determined gravimetrically.

(g) Free iron and aluminum - The oxalate extraction method outlined by McKeague and Day (1966) was used for removal of iron and aluminum oxides. Iron and aluminum in the extracts were determined colorimetrically.

(h) Exchangeable cations and exchange capacity - Exchangeable cations were extracted from the sample with 1 N ammonia acetate adjusted to pH 7.0 as outlined in A. O. A. C. (1955). Exchangeable potassium and sodium were determined with the Perkin Elmer model 303 Atomic Absorption Spectrophotometer. Calcium and magnesium were determined titrimetrically using standardized E. D. T. A. The cation exchange capacity was determined by extraction

of adsorbed ammonia with 1 N NaCl and distillation of the extract was carried out according to the method outlined in A.O.A.C. (1955).

(i) Exchange acidity - Exchange acidity was determined by leaching the soil with 0.5 N barium acetate adjusted to pH 7.0. The leachate was titrated with standardized sodium hydroxide as suggested by Brown (1943).

(j) Color measurements - Spectro-reflectance measurements were determined on Ah samples when air-dry and at field capacity. A Beckman model DU flame photometer with an adapted spectro-reflectance unit was employed for color measurements.

2. Organic analyses.

(a) Polysaccharide analysis -

(i) Hydrolysis : The method used for hydrolysis of the organic matter was a modification of the procedure presented by Brink (1960). Five grams of soil previously ground to pass a 1 mm mesh sieve was hydrolyzed with 50 ml 2 N H_2SO_4 at a constant temperature of $85^\circ C$ for 24 hours. Addition of water was necessary to compensate evaporation loss. The hot hydrolyzates were filtered through Buchner funnels washing the soil residue with 10 ml of hot water per gram of soil used. The filtrates were cooled to room temperature and brought to volume with distilled water and stored in the refrigerator.

(ii) Hexose determination : Brink's (1960) method was employed for hexose determination. A 5 ml portion of the properly diluted hydrolyzate was treated with 10 ml sulphuric acid and anthrone solution (0.4 g anthrone dissolved in 100 ml reagent grade concentrated H_2SO_4). The concentration of the soil hydrolyzate was determined colorimetrically using glucose for the standard curve.

(iii) Pentose determination: Pentose analysis was carried out on the hydrolyzate using the method outlined by Tracey (1950). d-(+)-xylose was used for the standard curve.

(iv) Uronic acid determination : The uronic acid sugars were determined using the method outlined by Lynch et al. (1957), as modified by Bitter and Ewins (1961). Carbazole was used to develop the color.

(b) Humic acid analysis -

(i) Extraction and preparation : Humic acid was extracted from the pooled* Ah₂ horizons using the method described by Kononova (1966). A weight of 200 g of soil was treated with 2 liters of 0.1 M sodium pyrophosphate + 0.1 M sodium hydroxide solution for 24 hours. The solution containing soluble humate was decanted and centrifuged at 9000 rpm for 1 hour. The centrifugate was decanted into beakers and HCl was added until the pH reached 2.4. The precipitated humic

* as described in Section 3(a)

acid was washed with dilute HCl into dialysis bags which were then placed into 2 quart jars and filled with distilled water. A second dialysis bag containing Dowex 50W-X8 in the hydrogen form was added to each container. Dialysis was continued for 10 days with 2 day intervals between water changes and resin regeneration. After dialysis, the purified humic acid was freeze-dried and stored in air tight vials.

(ii) Functional group analysis : Dragunova's method as stated by Kononova (1966) using BaCl_2 was employed for total functional group determination. Kukharensko's method as quoted by Kononova (1966) was used for the determination of carboxylic groups in humic acid.

(iii) E.M. and I.R. analysis : Methods for electron microscopic and infrared analysis of humic acid are the same as in Section 3(d) and 3(f).

3. Mineralogical analyses.

(a) Preparation of clay samples - Separation of total clay (less than 2 micron fraction) from the Ah_1 , Ah_2 and B horizons was achieved by gravity sedimentation. Mechanical dispersion was the only treatment performed on the above mentioned horizons. The separation of clay from sand and silt was accomplished by repeated decantation of the upper 10 cm of suspension after standing 10 hours.

Soil from the C horizon was mechanically dispersed, then treated with 5 N HCl to a pH of 5.0 to destroy carbonates. After all carbonates had been destroyed, the pH was readjusted to neutrality with NaOH. Total clay was separated as described above. The clay fraction was flocculated with CaCl_2 followed by washing with distilled water until chloride-free.

The total clay fraction from the B and C horizons was freeze-dried and stored in vials.

The suspended total clay fraction from the Ah_2 horizon was pooled so that all 4 sites within one area constituted one sample. Thus 3 clay samples were obtained for the Ah_2 horizons; one sample for each of the three major sampling areas. Similar pooling was conducted for the Ah_1 samples.

From the pooled samples, the 2-1 micron, 1-.2 micron, and .2-.08 micron fractions were separated using a Sorvall RC-2 supercentrifuge with a centrifuge speed and time calculated by Stokes law in the integrated form as proposed by Svedberg and Nichols (Jackson, 1955). Following fractionation, the clay fractions were immediately freeze-dried and stored in vials.

One third of each clay fraction from the Ah_2 horizon was treated with concentrated hydrogen peroxide over a steam bath until no reaction was visible. Of the remaining clay, one half of each sample was treated with a solution of 0.1 M NaOH + 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ (pH 13) for 24 hours. Excess NaOH- $\text{Na}_4\text{P}_2\text{O}_7$ was removed

by successive washings with distilled water. The remaining clay was called the untreated clay. All fractions were immediately freeze-dried and stored in suitable containers.

(b) X-ray analysis of clay minerals - The clay samples were prepared for x-ray analysis according to the method of Kittrich (1961). A few drops of clay suspension were placed on glass slides and allowed to dry by standing overnight. The clay samples were glycolated by placing the prepared slides in a saturated atmosphere of ethylene glycol in a 60° C oven for 48 hours. Duplicates of the glycolated slides of these samples were heated to 550° C for 2 hours before running the x-rays. An additional treatment was performed on C horizon clays which consisted of saturation with 1 N NH_4Cl followed by a 300° C heat treatment for 1 hour.

A Philips x-ray diffractometer with a high angle goniometer was used for x-ray analysis of the clays. The x-ray generator was set at 40 kilovolts, 20 milliamperes using $\text{CuK}\alpha$ radiation with a nickel filter. Slit sizes used were 1°, .1 mm, and 1° with a scanning speed of one degree 2θ per minute. Chart speed was set at 1 cm per minute.

Recorder settings were as follows:

Clay fraction	Clay treatment	Slide treatment	Recorder settings		
			CPS	TC	ZS
total clay	-	glycolated	400	8	0
C horizon	-	heated 550° C	200	8	0
	NH ₄ saturation	heated 300° C	400	8	0
total clay	-	glycolated	400	4	0
B horizon	-	heated 550° C	200	8	0
Ah ₂ clay	-	glycolated	200	8	0
all fractions	-	heated 550° C	200	8	0
	H ₂ O ₂	glycolated	200	8	0
	H ₂ O ₂	heated 550° C	200	8	0
	NaOH-Na ₄ P ₂ O ₇	glycolated	200	8	0
	NaOH-Na ₄ P ₂ O ₇	heated 550° C	200	8	0

(c) Differential thermal analysis - An Aminco Thermal Analyzer model 4-4442 was used for differential thermal analysis of clays. Freeze-dried clays were passed through a 300 mesh sieve and packed into the furnace. In the case of Ah₂ clay fractions which were in the untreated or pyrophosphate treated form, 50% by weight of ignited Al₂O₃ was added and thoroughly mixed with clay before furnace loading. Temperature rise was set at 16° C per minute, thermocouple sensitivity was set at 0.5° C per inch differential, and recorder sensitivity was set at 5 millivolts per division for the X axis and 1 millivolt per division for the Y axis. When nitrogen atmosphere was used, a flow rate of 40 cc/min was employed.

(d) Infrared analysis - Three milligrams of sample were mixed with 1 g KBr and compressed into a disc 0.95 mm thick. The infrared spectra of clays and humic acid were recorded on a Perkin Elmer

Model 221-1600 infrared spectrophotometer with a prism-grating interchange.

(e) pH dependent and independent C.E.C. - For the total C.E.C. determinations 0.5 g samples were extracted with 3 successive portions (25 ml) of 2 N $\text{CaCl}_2 + \text{NH}_4\text{OH}$ adjusted to pH 10.0, using 2 hour shaking intervals except for the third one when the mixture was shaken overnight. The samples were washed free of Cl^- with a water and alcohol solution using the centrifuge and then extracted with two treatments of 1 N BaCl_2 . The extracted Ca was determined on a Perkin Elmer Model 303 atomic absorption spectrophotometer.

pH independent C.E.C. was determined by treating 0.5 g samples with 3 successive portions (25 ml) of 2 N $\text{KCl} + \text{HCl}$ adjusted at pH 3.0. The samples were washed free of chlorides with water and water and alcohol solutions. Potassium was replaced by 3 successive washings of 1 N CaCl_2 and determined by the atomic absorption spectrophotometer.

pH dependent C.E.C. was calculated as the difference between total C.E.C. and pH independent C.E.C.

(f) Electron microscopic analysis - For electron microscopic examinations, clay samples were prepared as a 0.01% suspension in distilled water. Humic acid samples were prepared by diluting samples taken from the dialysis bag until a suitable grid density of humic acid was obtained. The diluting solution used was distilled water

+ HCl (pH 6) for humic acid samples.

The samples were sprayed onto a formvar film supported on a 300 mesh per inch copper grid. After air-drying the specimens were examined and photographed by using the Philips EM 100B and the Philips EM 200 electron microscope. For the Philips EM 100B a 60 kilovolt accelerator voltage was employed using P 426 film plate type. Eighty kilovolts accelerator voltage was used with the Philips EM 200 with a P 26 film plate type.

(g) Fe and Al determinations - About 0.7 g clay was extracted with acid ammonium oxalate for 4 hours. The extraction was carried out in the dark. Following extraction, the suspensions were centrifuged until a clear supernatant remained. An aliquot of the centrifugate was analyzed on the atomic absorption spectrophotometer for Al and Fe.

(h) Surface area - Surface area was determined using the method outlined by Heilman et al. (1965). Freeze dried clay samples were liquid saturated with ethylene glycol monoethyl ether and placed in the vacuum dessicator. A beaker containing CaCl_2 + ethylene glycol monoethyl ether was placed in the dessicator along with the sample. A vacuum of 27 p.s.i.g. was applied for a time determined by the surface area value obtained for standard calcium saturated Arizona montmorillonite.

(i) K_2O content - For K_2O content 0.5 to 1 g of clay was treated

with two 10 ml volumes of HCl and HF (conc.) with intermittent evaporation to near dryness. After the second HCl and HF treatments, the residue was heated to dryness, treated with 5 ml of HCl and again heated to dryness. The residue was taken up in 5 per cent HCl and made to volume. Potassium concentration was determined with the Perkin Elmer Model 303 atomic absorption unit.

(j) C.E.C. of total clay from the Cca horizon - For the C.E.C. determinations 0.5 g samples were treated with 3 successive portions (40 ml) of 1 N sodium acetate, using 4 hour shaking intervals except for the third one when the mixture was shaken for 12 hours. The samples were washed free of excess sodium acetate with a water and alcohol solution using the centrifuge and then extracted with three treatments of 1 N ammonium acetate. The extracted Na was determined on the Perkin Elmer model 303 atomic absorption spectrophotometer.

4. Micropedological analysis.

(a) Field sampling - Undisturbed samples were obtained by spading out a large mass of soil followed by a trimming to obtain a soil clod that would fit into a padded 400 cc cardboard container. The sample was allowed to air dry in the containers after which clods of 30 to 35 cc were removed by knife trimming. Each small clod was placed in a 50 cc crucible with the natural orientation being

maintained. Impregnation of the clod was carried out in the 50 cc crucible.

(b) Impregnation - The method used for impregnation was that of Acton (1961) as modified by Dumanski (1964). The crucible containing the sample was placed in an oven and dried at 60° C for one-half hour prior to impregnation. The impregnation mixture consisted of 30 ml Castolite-X plus 8 ml of Castolite thinner per sample. Castolite-X and thinner were poured together in the proper amounts, heated to 55° C with constant stirring during the heating period. Upon reaching a temperature of 55° C, the mixture was removed from the heat source and Castolite hardener was added at the rate of 8 drops per 6 samples. After thorough stirring, this impregnating mixture was added to the crucibles until the clods were entirely covered. The crucibles were then placed in a vacuum chamber and suction was applied at a rate of one inch of mercury per minute with a total suction equivalent to 20 inches of mercury over a period of 20 minutes. Evacuation was terminated after one hour. The crucibles were then placed in a fume cupboard for 3 days to allow the impregnating medium to harden. The samples were then placed in the oven for 2 days at 60° C for final curing.

(c) Preparation of thin sections - A slice 1/4 inch thick, possessing the desired orientation, was cut from the cast using a

diamond saw. The edges of this slice were trimmed so that the chip would fit on a 3 x 1 inch microscopic glass slide with no clear Castolite remaining as part of the chip. The most uniform side of the chip was polished as smooth as possible using 320 grit silicon carbide abrasive powder on a lapidary followed by grinding with 600 grit silicon carbide on a double diamond glass plate. Following grinding, the chip was thoroughly cleaned with varsol. A glass slide was placed on a hot plate at 135° C and a bar of Lakeside 70 c thermoplastic cement was held on the slide until the required amount had melted off. The slide was left on the hot plate for 6-10 seconds; if bubbles appeared a new slide was prepared. The chip, smooth side down, was placed on the slide and gentle pressure was used to force most of the Lakeside 70 from beneath the chip. The glass slide with chip was quickly removed from the hot plate and placed chip down on a smooth surface. With the aid of a pencil, moderate pressure was applied to the glass slide above the middle of the chip while at the same time, rapid lateral movement of the glass slide was carried out before the Lakeside 70 commenced setting. In this manner, bubble free mounts could be obtained with relative ease.

An oil bath diamond saw was used for the final trimming. The thickness of the chip after the final trimming was 0.06 mm. A final grinding on a double diamond glass plate was used to reduce the thickness of the thin section to 0.03 mm. Interference colors

produced by quartz grains were used as a guide in thickness estimation. When the final grinding was completed, the slide was thoroughly washed in varsol and dried with tissue.

Cover slips were mounted on the dry thin sections using Permunt. A small band of Permunt was placed centrally on the cold thin section and a cover slip was placed on top. With the aid of a pencil gentle pressure was applied to the cover slip until all bubbles were freed and excess mounting medium was forced to the edges. The slides were then allowed to set for 48 hours. The prepared thin section was now ready for petrographic investigations.

(d) Photography - A Carl Zeiss model 51871 photomicroscope was used for photographing thin sections. Kodak High Speed Ektachrome type B film was used in the camera. Two D50 gray filters were used over the artificial light source. Film speed setting was kept at 7 for the above mentioned film and light settings varied between VII and X depending on the field illumination. The auxillary ring lens was set at 1.25 X, the ocular lens was set at 3.2 X and 6.3 X and 3.2 X objective lenses were employed.

IV. RESULTS AND DISCUSSION

Thin Sections

Thin sections of the Ah₁ and Ah₂ horizons were prepared and examined to determine whether or not differences in the microstructure exist among the chernozems from the three sampling areas. Typical photomicrographs are presented (Plates 1 to 6).

The terms used to describe the photomicrographs were adopted from the published material of Kubiena (1938) and Brewer (1964) who defined them as follows:

"Plasma of a soil material is that part which is capable of being or has been moved, reorganized, and/or concentrated by the processes of soil formation. It includes all the material, mineral or organic, of colloidal size and relatively soluble material which is not bound up in skeleton grains."

"Skeleton grains of a soil material are individual grains which are relatively stable and not readily translocated, concentrated or reorganized by soil-forming processes."

"Soil fabric is the arrangement of the constituents of a soil in relation to each other."

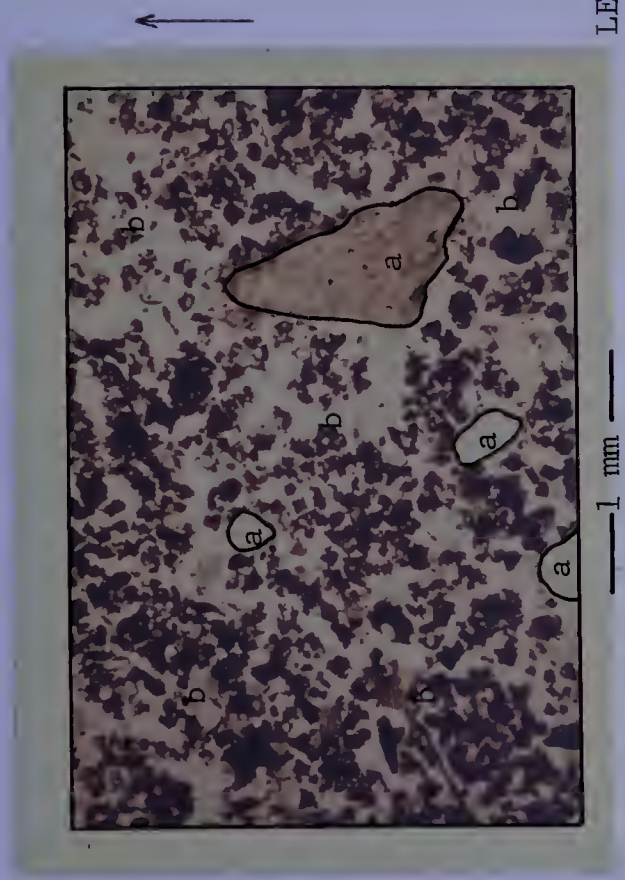
"Soil matrix consists of the plasma, skeleton grains, and voids that do not occur in pedological features other than plasma separations."

Examination of the prepared thin sections revealed a significant difference in the microstructure of the Ah horizons found in the Pincher

Creek area as compared to Ah horizons found in the Olds and Edmonton sampling areas. The thin sections show that for the Ah₁ and Ah₂ horizons from the Pincher Creek sampling area, the microstructure consists of individual spherical granules of plasmic material varying from 0.1 to 0.4 millimeters in diameter. In addition the skeleton grains are loosely bound or unbound to each other and to plasmic material.

In the Edmonton and Olds sampling areas, the Ah horizons were found to possess a fabric similar to that described by Kubiena (1938), St. Arnaud (1964) and Pettapiece (1964) as chernozemic or spongy fabric. The skeleton grains were imbedded in a porous groundmass of plasmic material high in decomposed organic matter or in some cases the mineral grains were closely surrounded and bound together by the organic fraction of the soil. The microstructure of the Ah horizons obtained from the Edmonton and Olds areas consisted of irregularly shaped, organic-rich aggregates varying from 0.2 to 1.0 millimeters or greater in diameter.

In many respects, the microscopic appearance of the Ah horizons from the soil in the Pincher Creek area is similar to mull-like moder as described by Kubiena (1953) where the humus and mineral particles are present as distinctly separable elements. In contrast, the microscopic appearance of the Ah horizons from the soil in the Olds and Edmonton sampling areas is similar to that described by Kubiena (1953) as mull humus.



plane light



polarized light

LEGEND
a). large minerals
b). voids and matrix

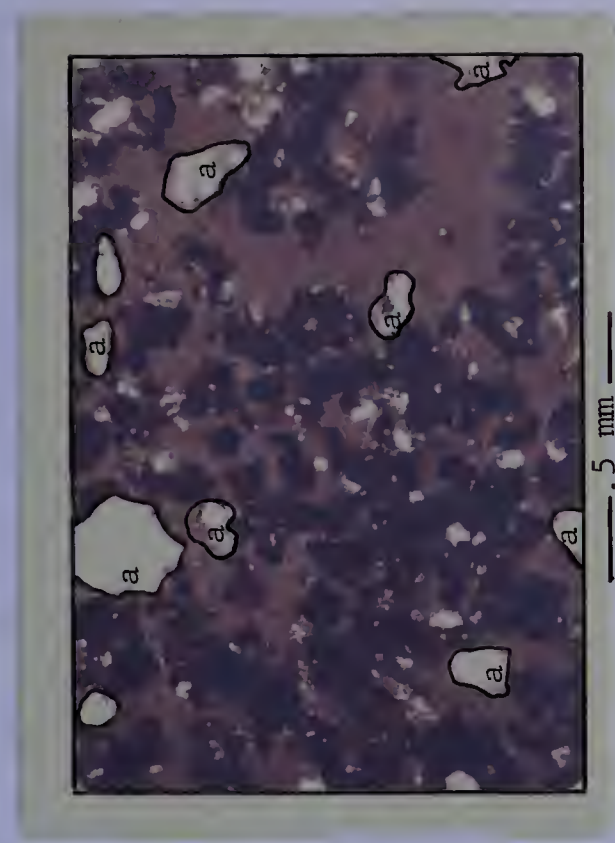
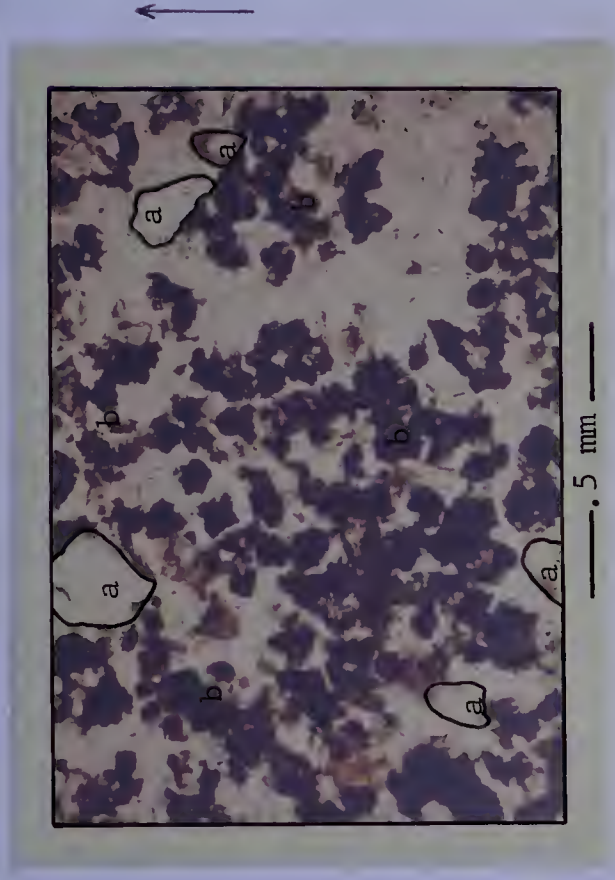
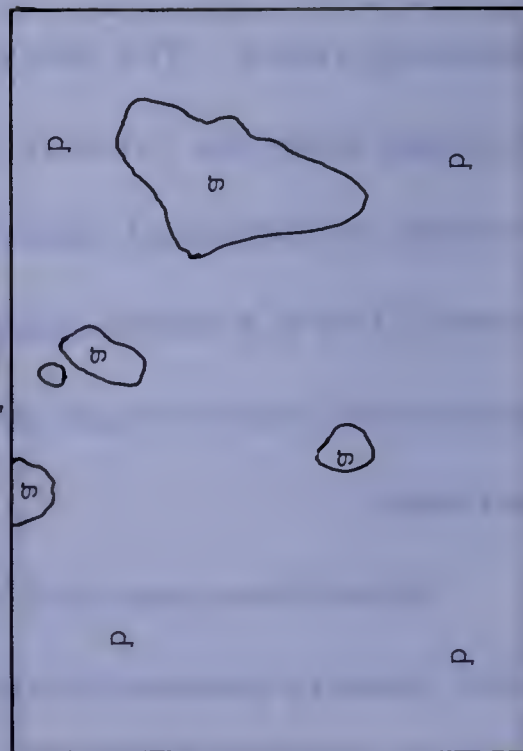
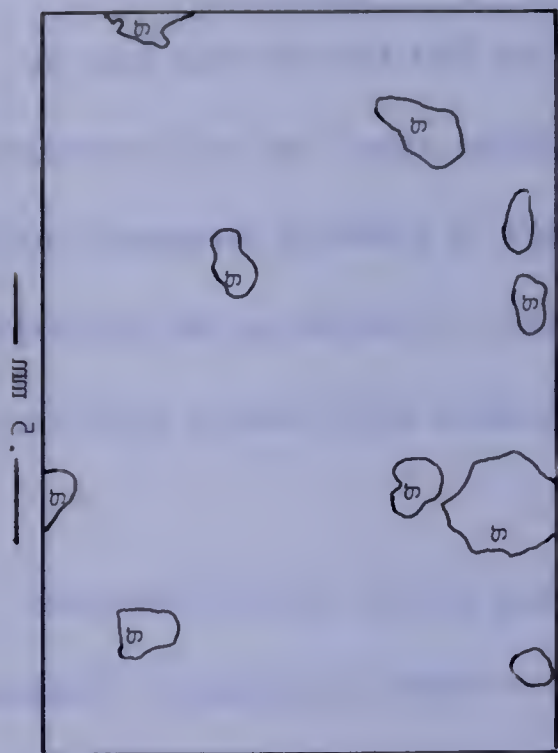
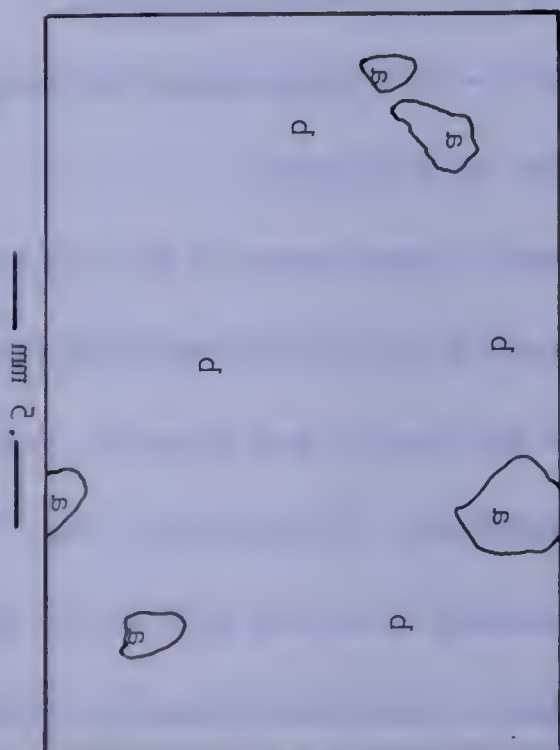
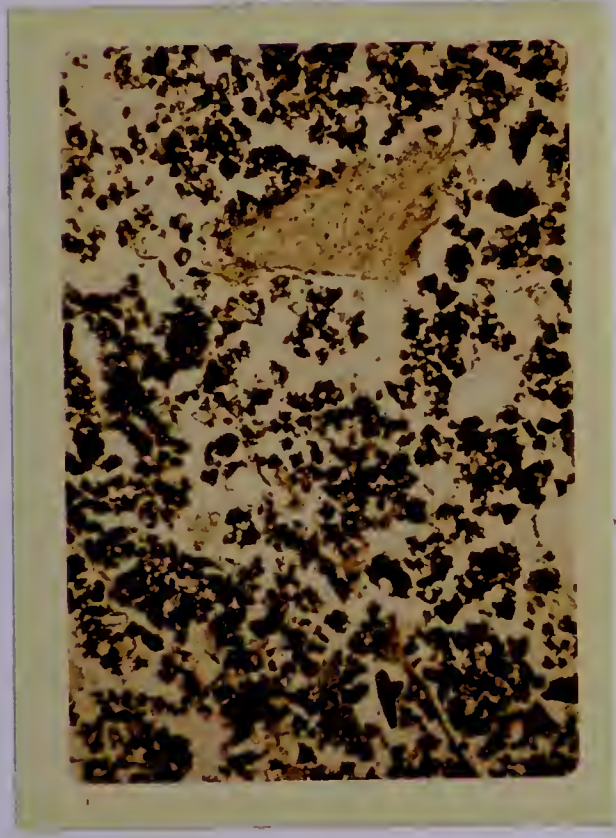


Plate 1. Photomicrographs of the Ah₁ horizon from the Pincher Creek sampling area.

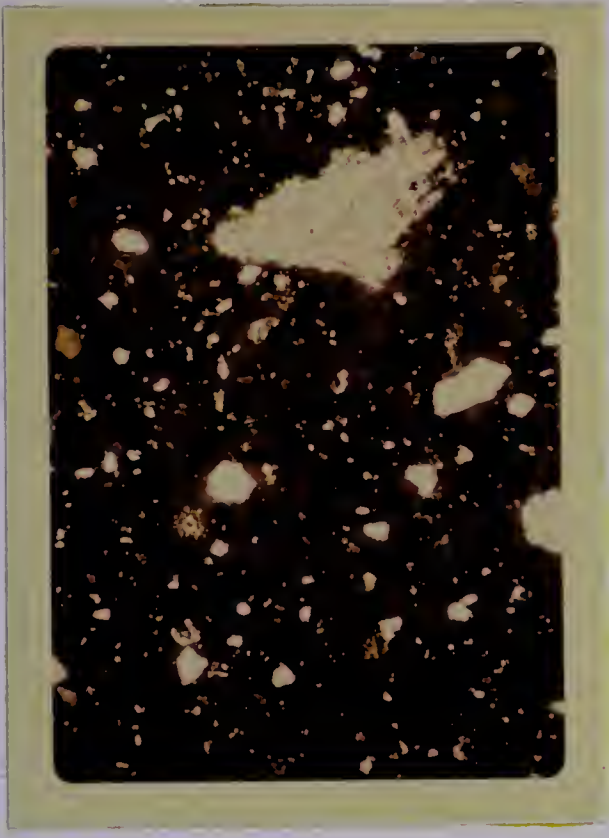
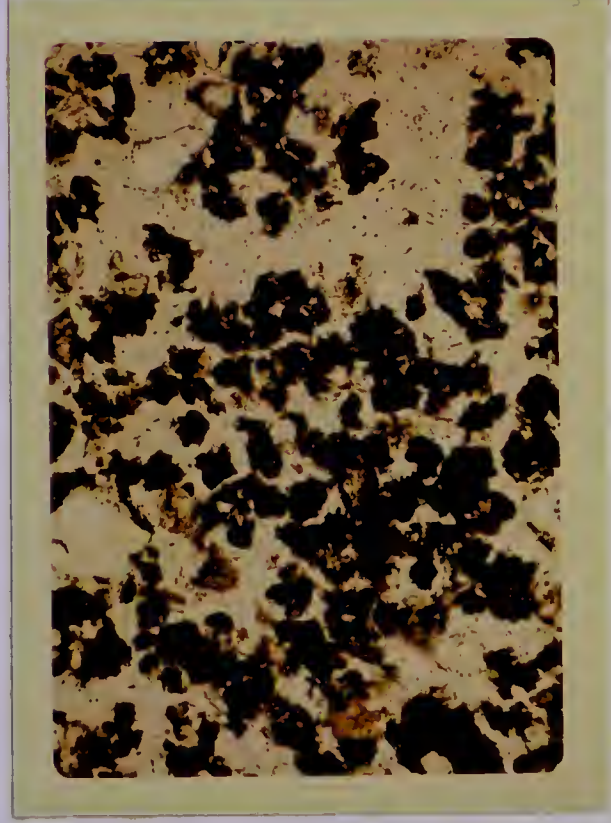


p). voids and matrix
s). large minerals
LEGEND





plane light



polarized light

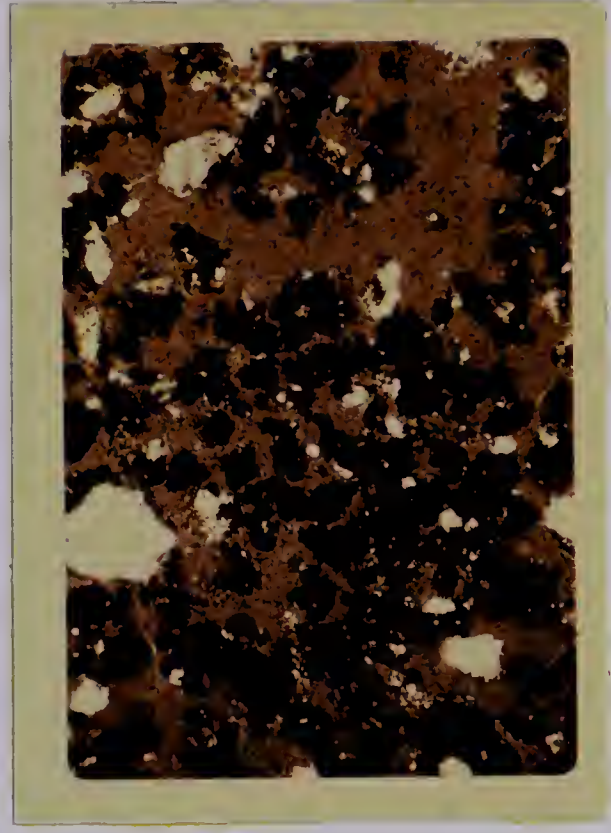


Plate 1. Photomicrographs of the Ah₁ horizon from the Pincher Creek sampling area.

Description of Plate 1

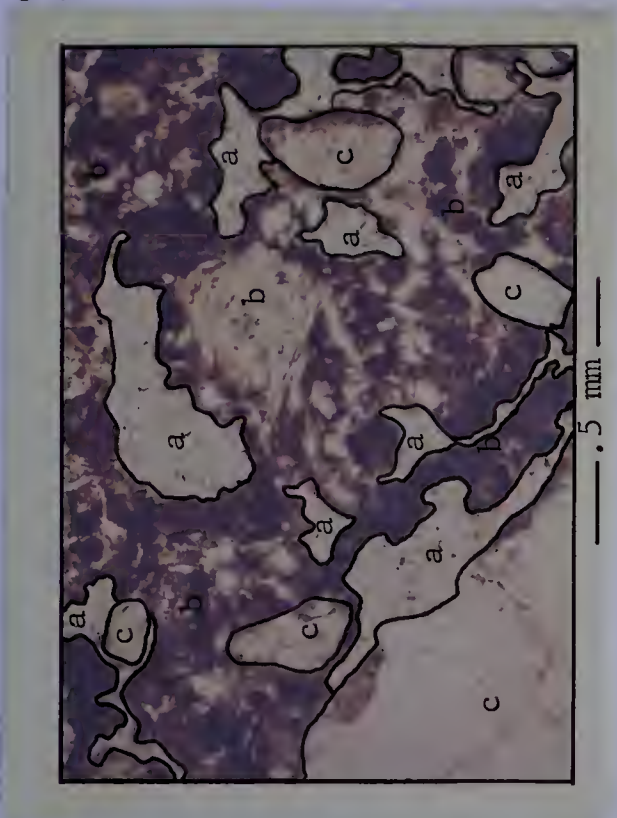
The pictures comprising Plate 1 illustrate the structure of the Ah₁ horizons in the Pincher Creek sampling area. The salient feature of the Ah₁ horizon is the formation of micro-granules approximately 0.1 mm to 0.4 mm in diameter. In addition, the micro-granules are almost entirely plasmic in composition with skeleton grains existing as individual entities. Except for very thin organic coatings, the mineral grains show very little association with the plasmic organic granules. The skeleton grains or plasma is evident. This type of fabric has been described as "modified chernozemic" by Dumanski et al. (1966).



plane light

LEGEND

- a). voids
- b). matrix
- c). large minerals
- d). voids and matrix



polarized light

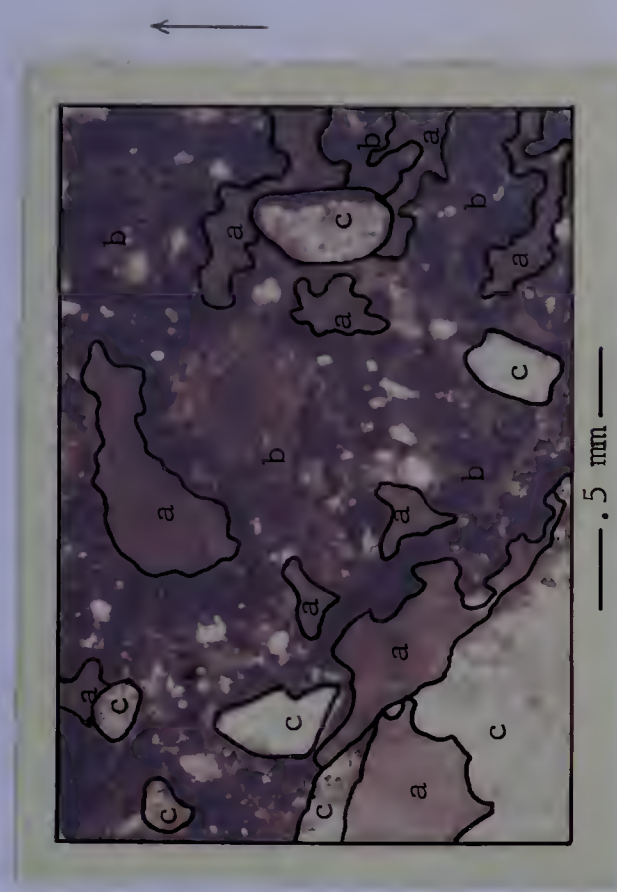
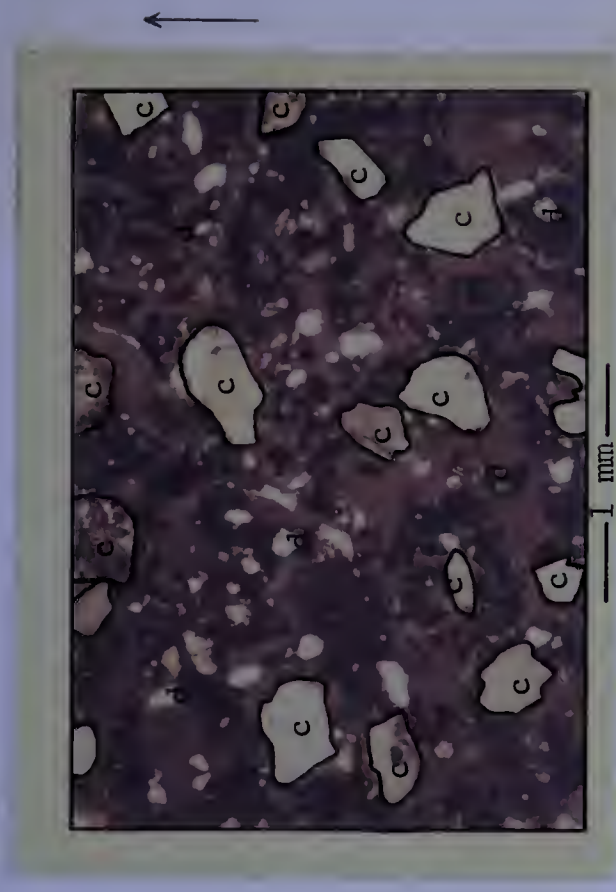
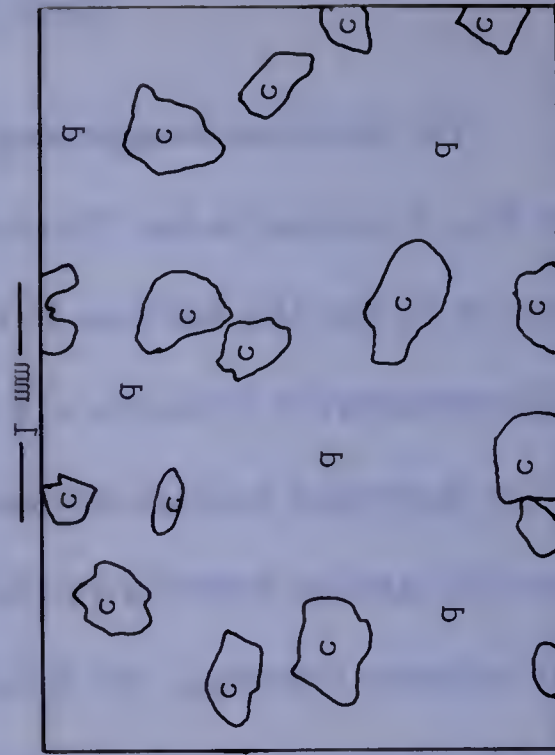
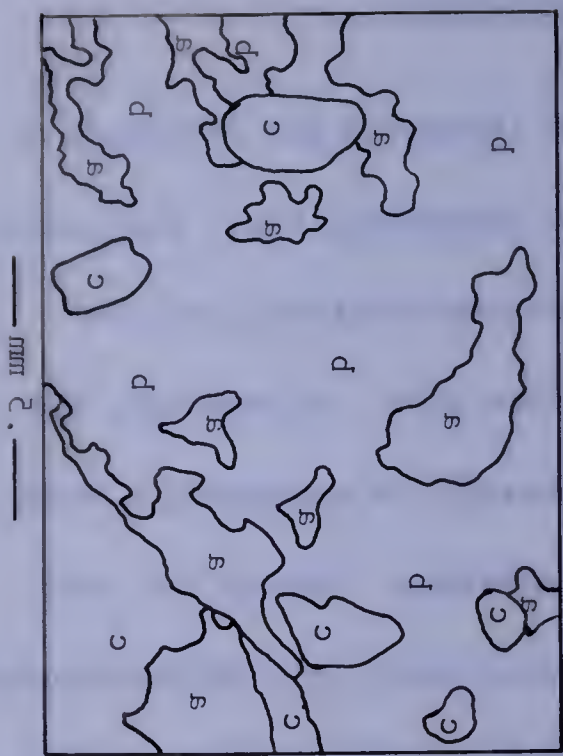
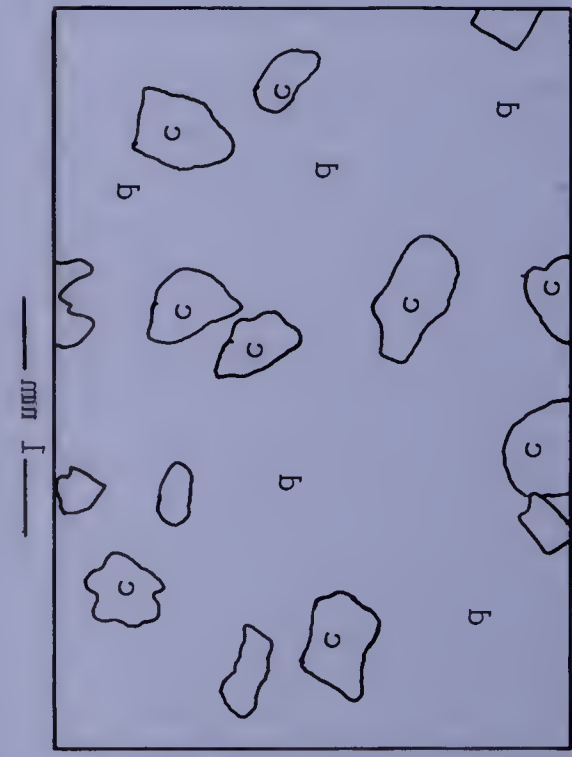
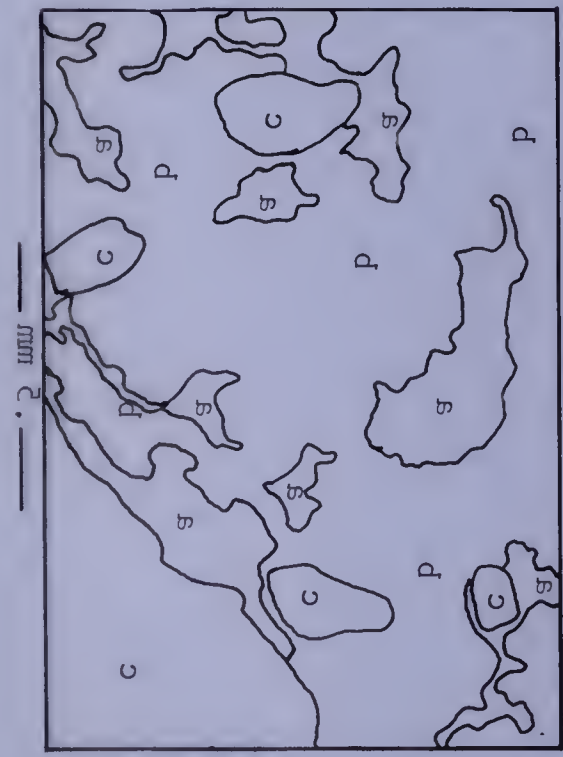
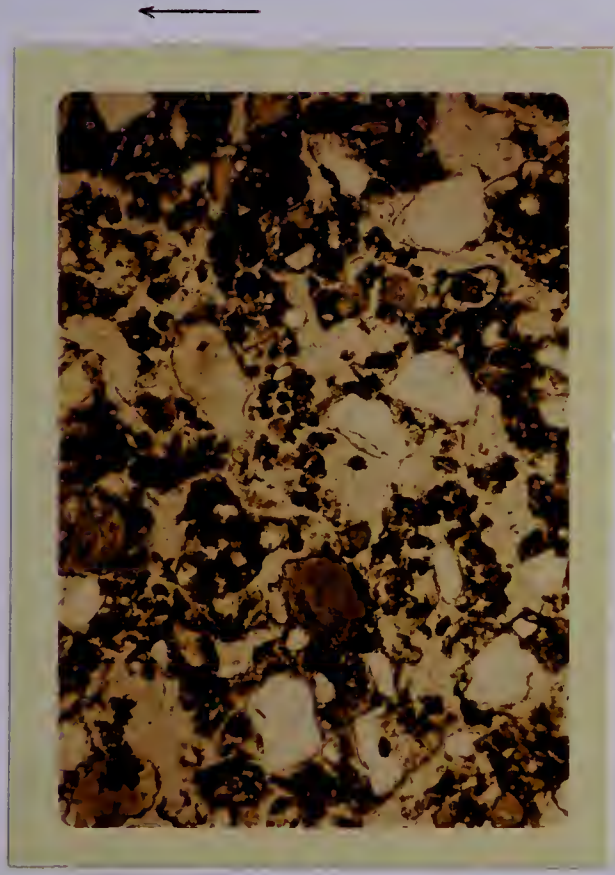


Plate 2. Photomicrographs of the Ah₂ horizon from the Pincher Creek sampling area.

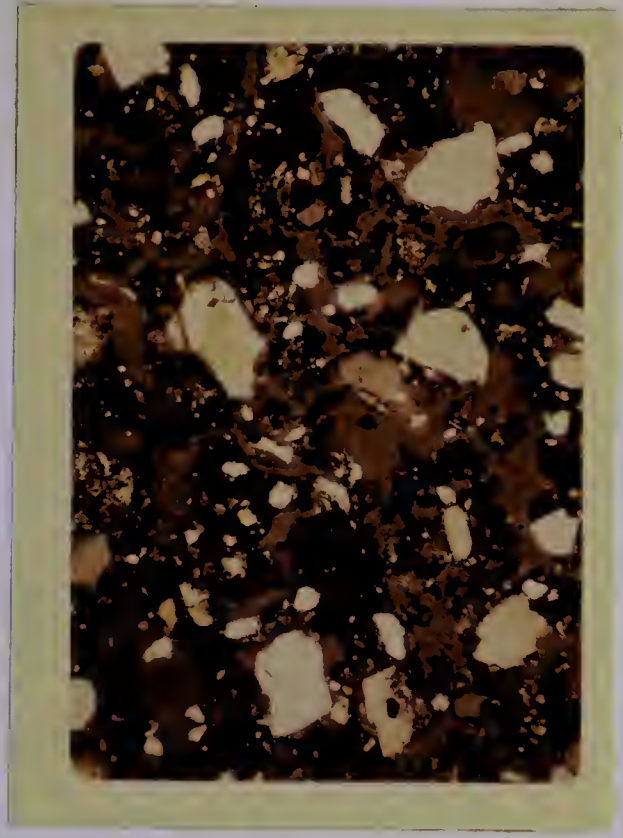


q). voids and matrix
 c). large minerals
 p). matrix
 s). voids
 LEGEND





plane light



polarized light

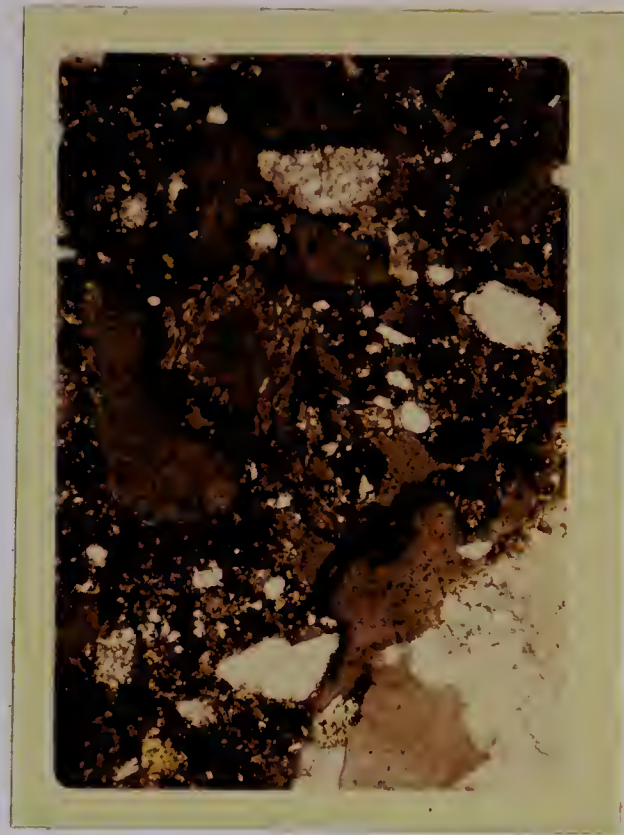
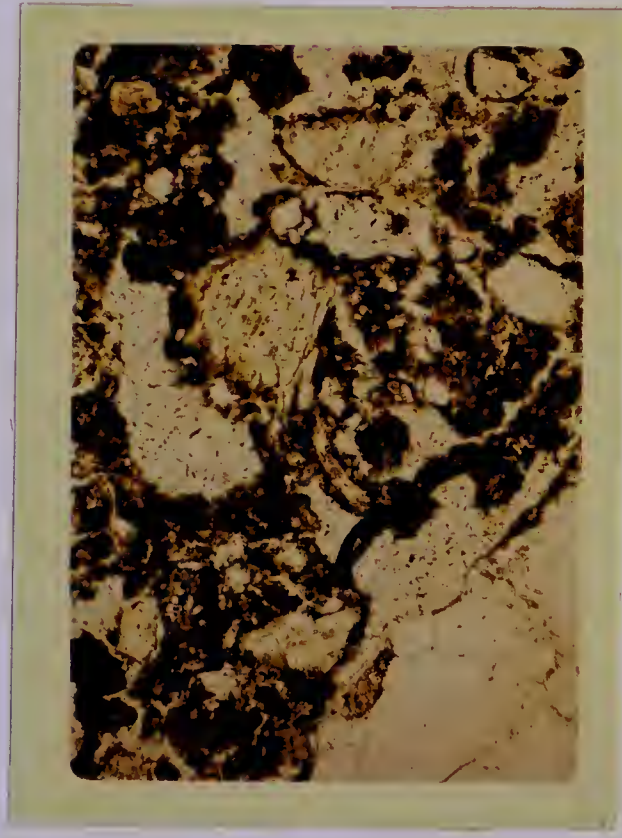
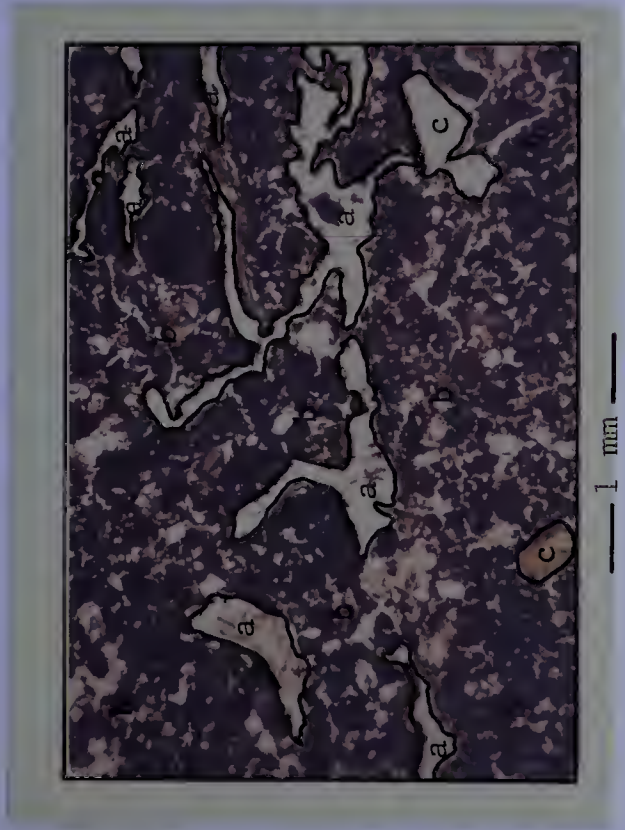


Plate 2. Photomicrographs of the Ah₂ horizon from the Pincher Creek sampling area.

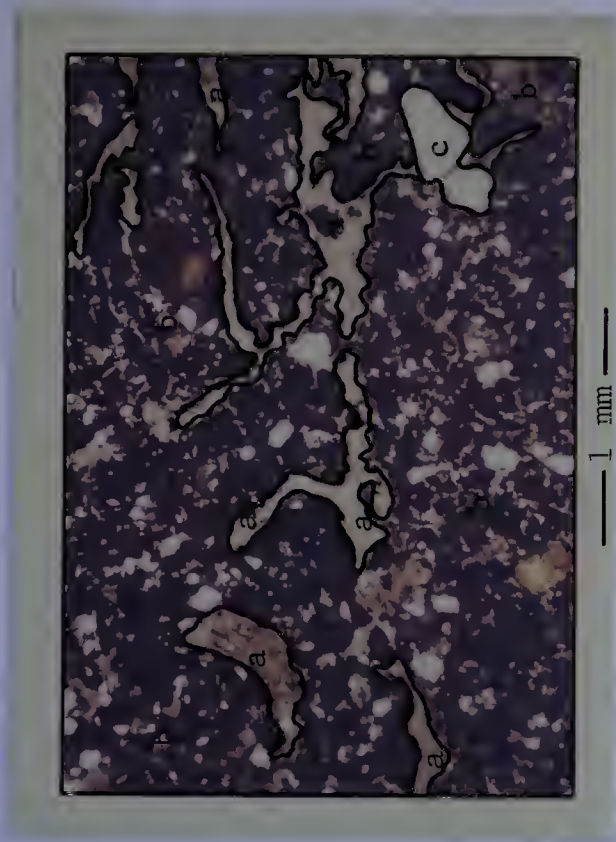
Description of Plate 2

Plate 2 contains photomicrographs of thin sections representing the Ah₂ horizons from the Pincher Creek area. There is a decrease in the individuality of plasmic organic granules and skeleton grains when a comparison is made to Plate 1. Many of the larger mineral grains exist as separate entities but more of the smaller minerals are intimately associated with organic plasmic material. Under high magnification, organic coatings on the large minerals appear more prominent with intergranular braces uniting some of these larger grains to the plasmic material and to other mineral grains. No orientation was observed in Plate 2. This type of fabric would still be "modified chernozemic" but tending toward "chernozemic" as defined by Kubiena (1938).



plane light

— 1 mm —



polarized light

— 1 mm —

LEGEND

- a). voids
- b). matrix
- c). large minerals

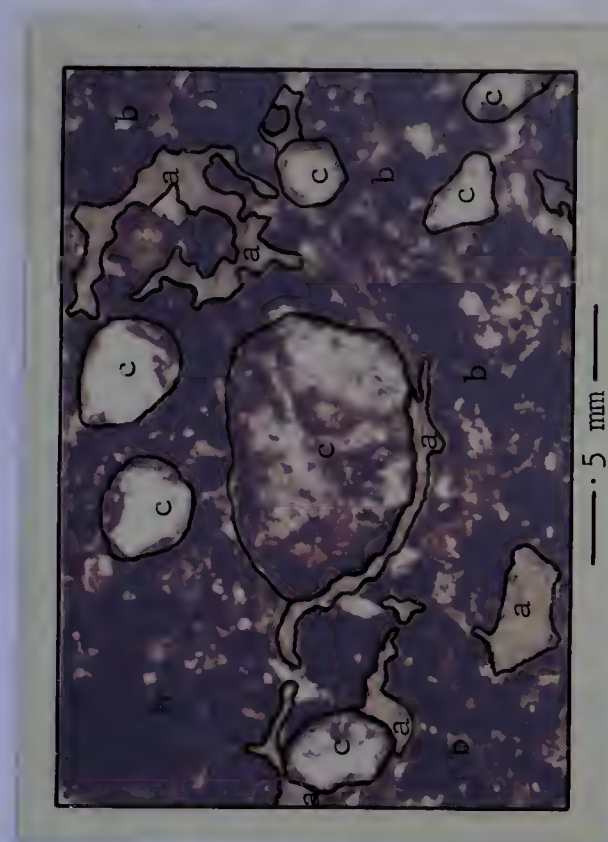
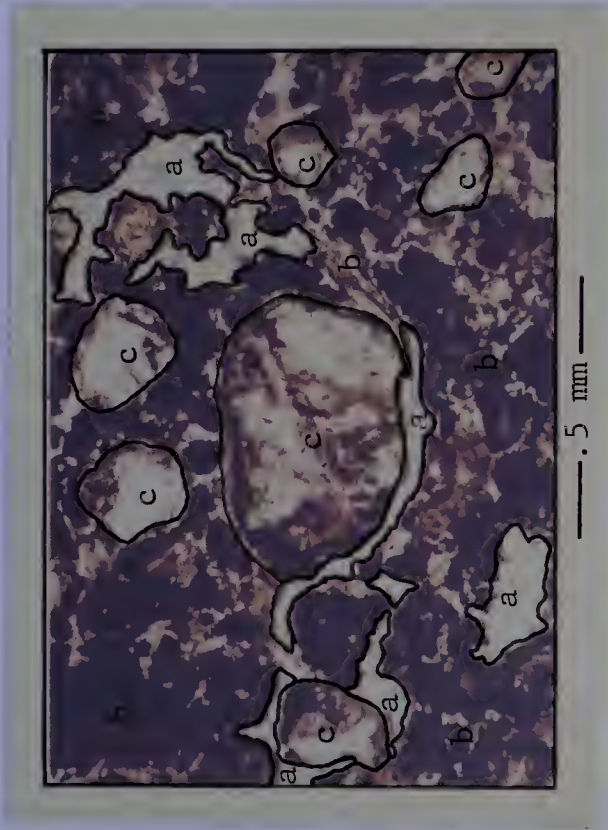
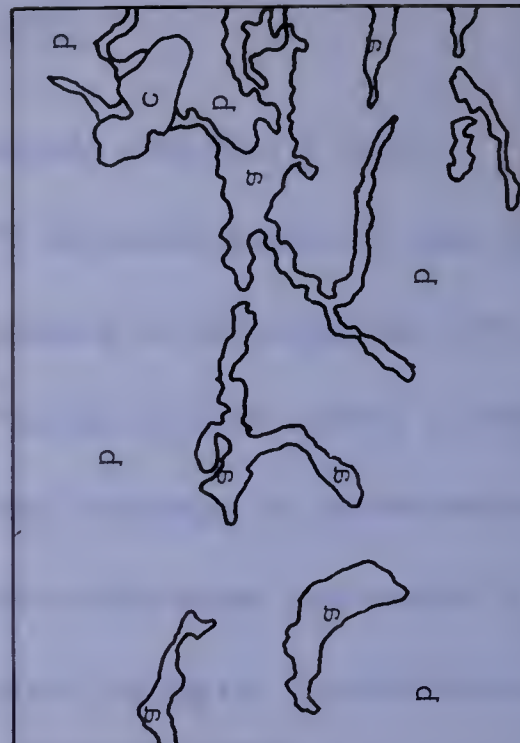
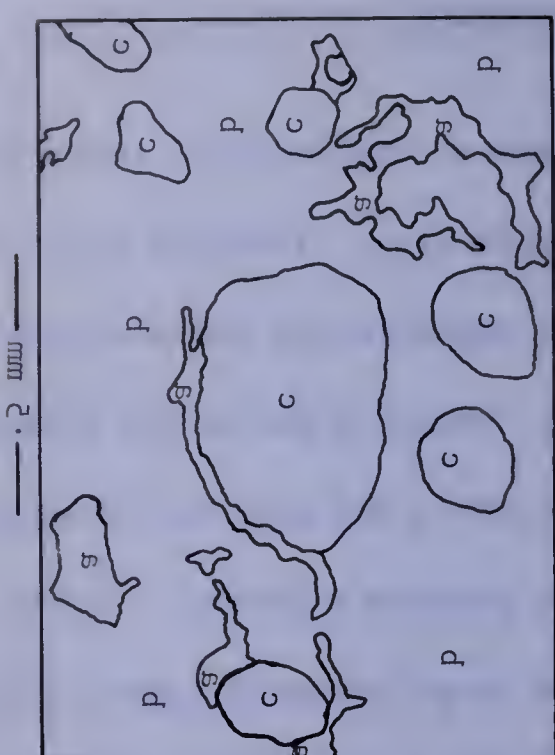
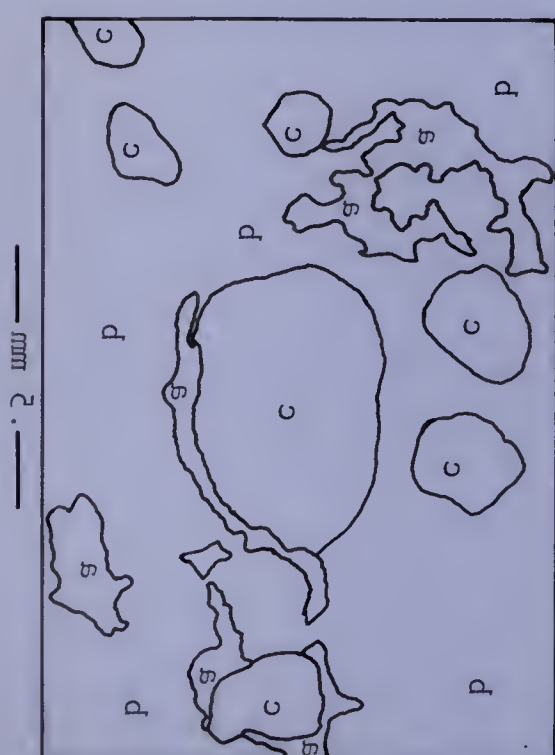
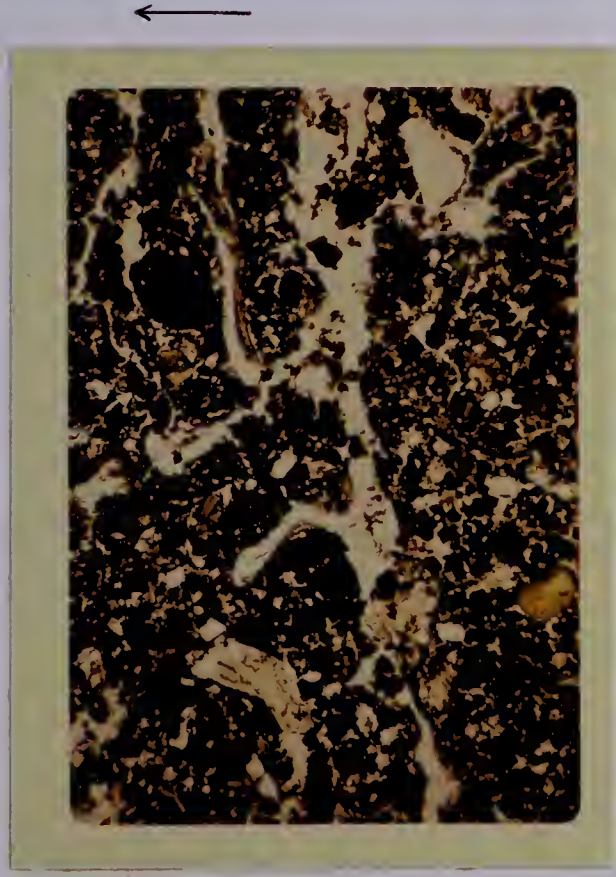


Plate 3. Photomicrographs of the Ah₁ horizon from the Olds sampling area.

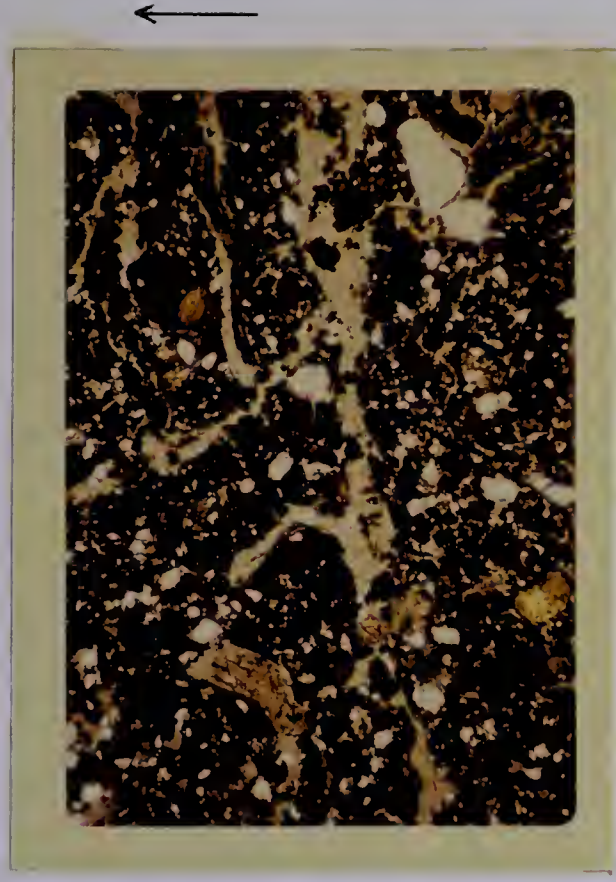


c). large minerals
 p). matrix
 s). veins
 LEGEND





plane light



polarized light

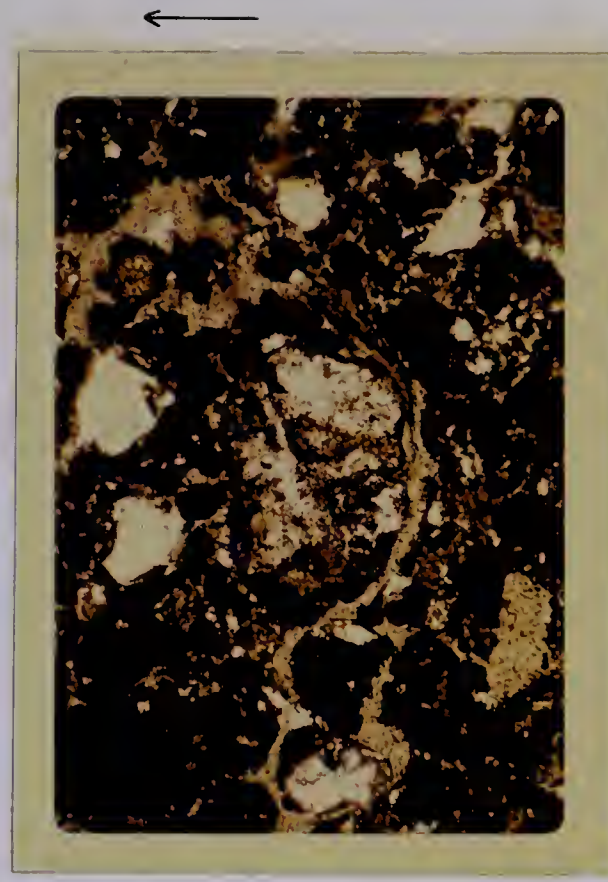
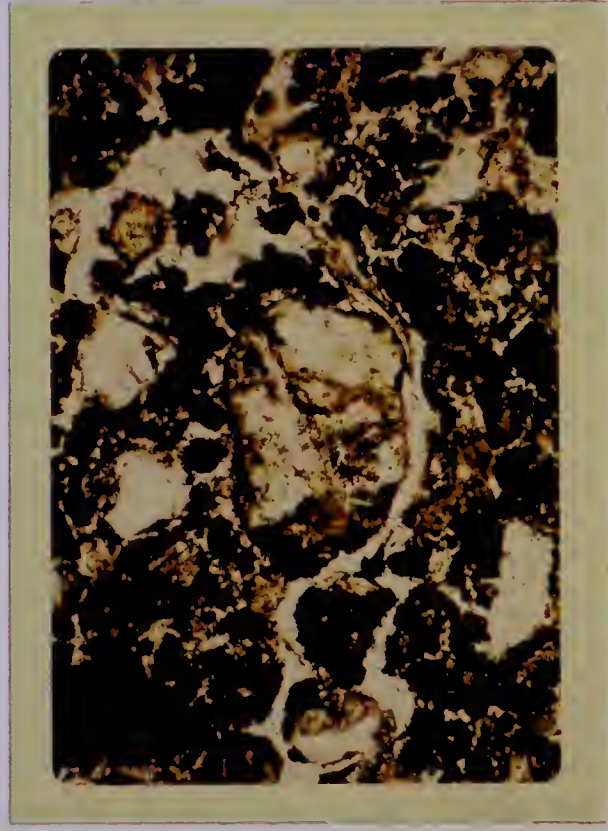
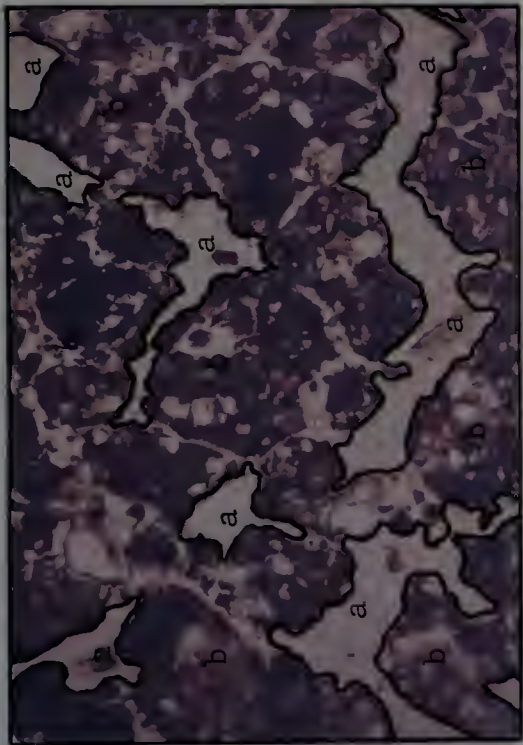


Plate 3. Photomicrographs of the Ah₁ horizon from the Olds sampling area.

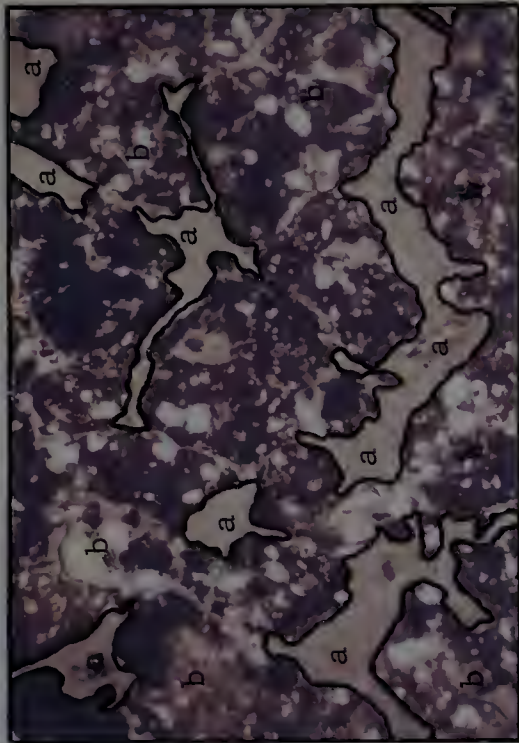
Description of Plate 3

Characteristics of the Ah₁ horizons from the Olds area are illustrated in Plate 3. The salient feature depicted by the photographs is the intimate association of skeletal grains and plasma forming a dense matrix. Mineral grains are completely engulfed or incorporated into the plasma with pronounced staining and linkages. The horizontal voids appearing in the top photographs are felt to be due to slight compaction of the Ah₁ horizon. The photographs illustrate that organic matter is decomposed to the extent that no discernible plant structures are evident. The plasma is in micro-granular form much the same as in Plate 1 but the granules are all linked together and to mineral grains having the appearance at times of dense plasmic masses. According to Kubiéna (1938) and Pettapiece (1964) the fabric is "chernozemic".



1 mm

plane light

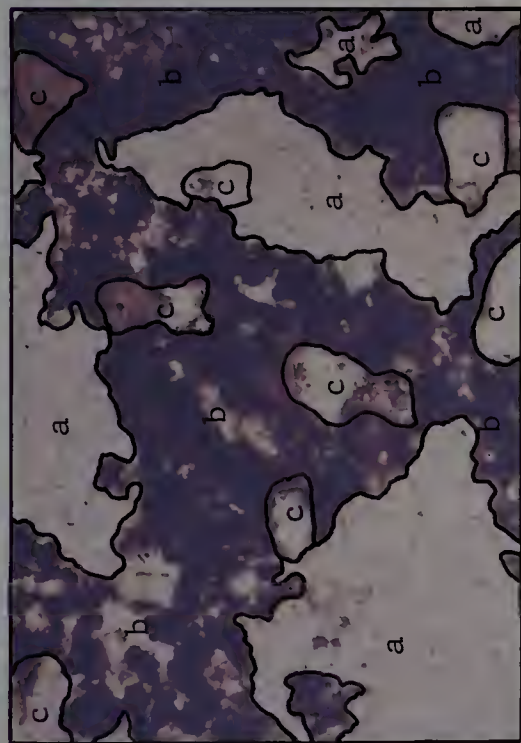


1 mm

polarized light

LEGEND

- a). voids
- b). matrix
- c). large minerals

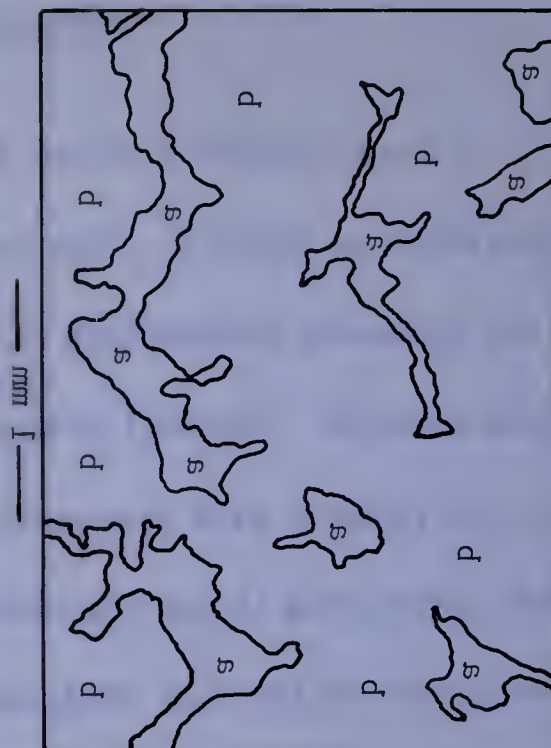
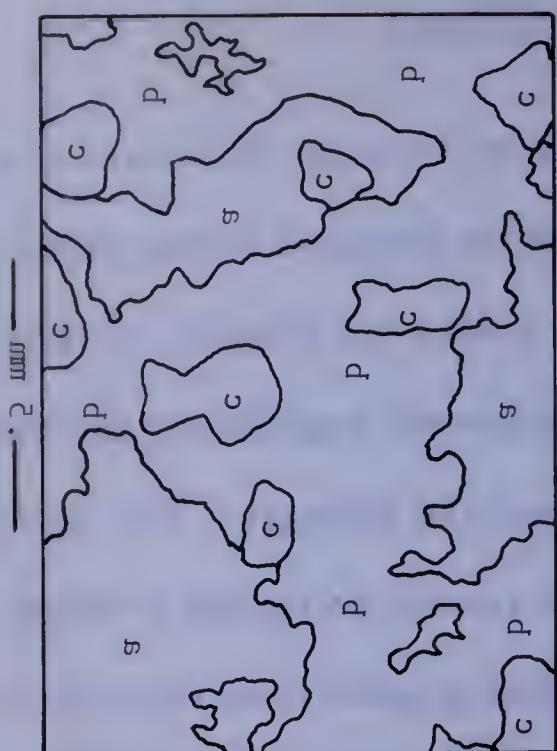


0.5 mm

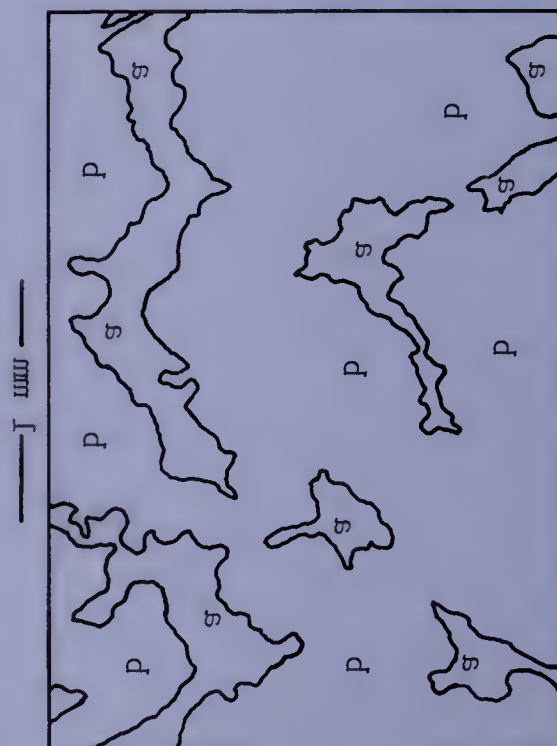
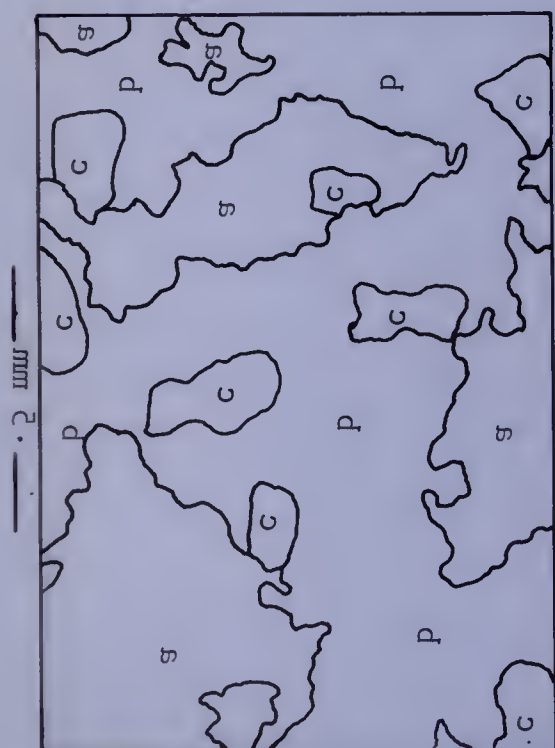


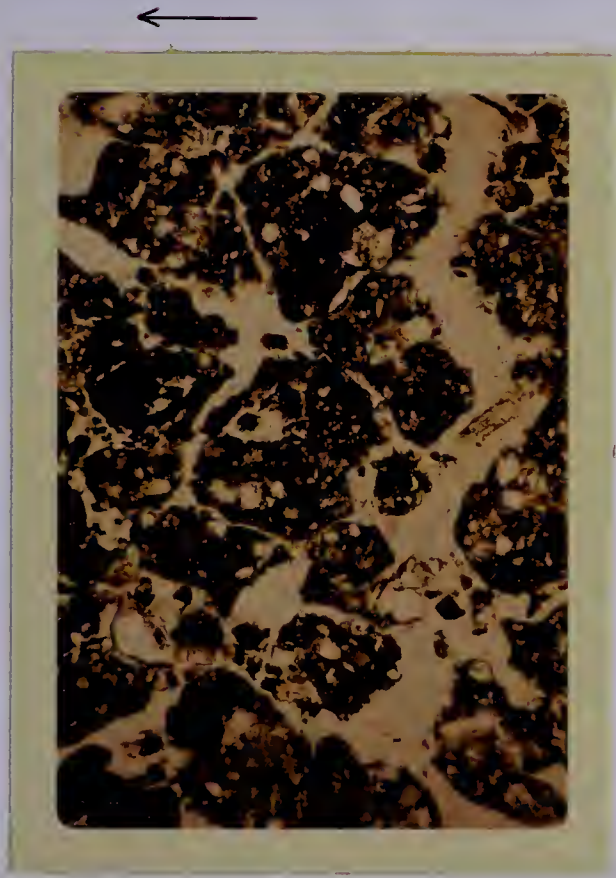
0.5 mm

Plate 4. Photomicrographs of the Ah₂ horizon from the Olds sampling area.

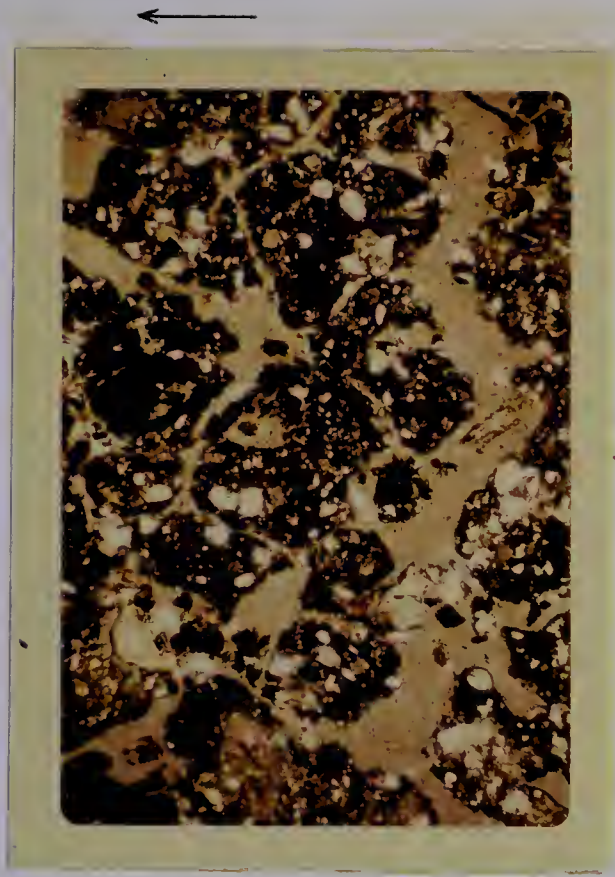


c). large winged insects
 p). water
 s). air
 LEGEND





plane light



polarized light

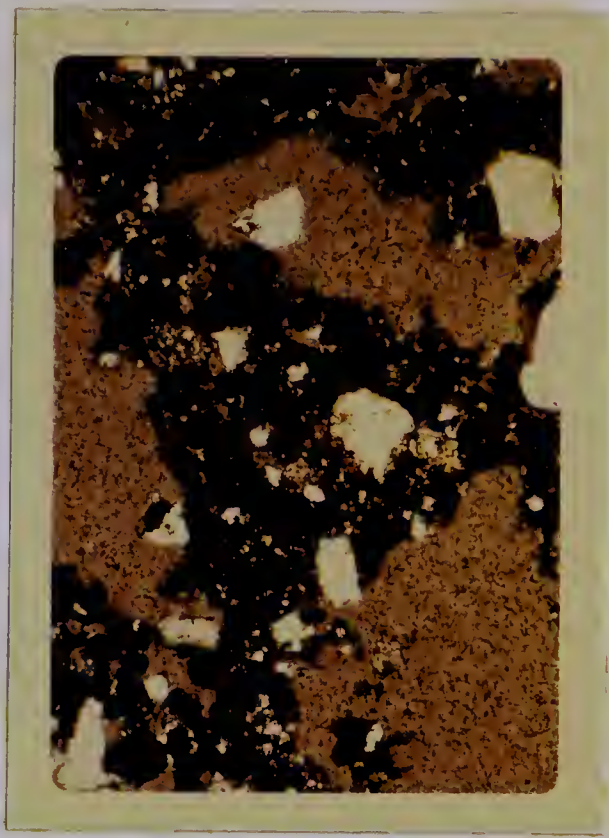
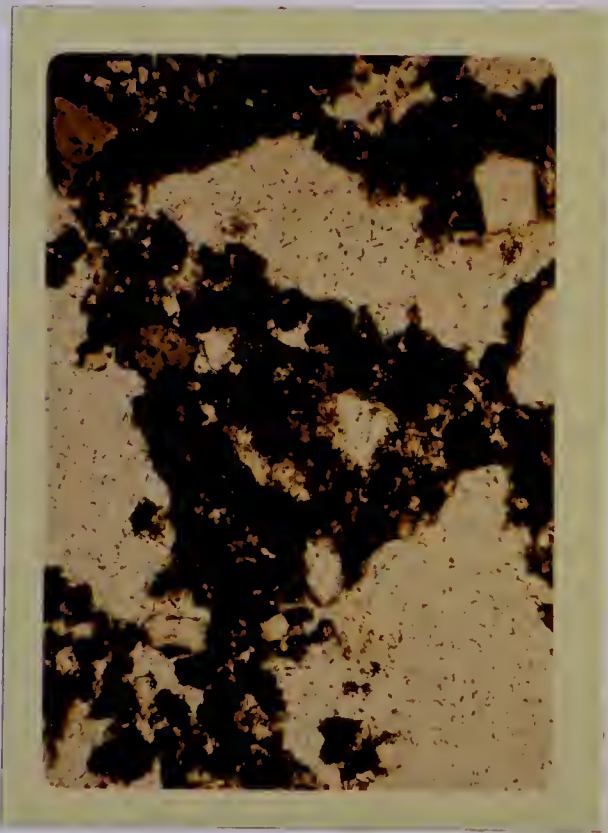
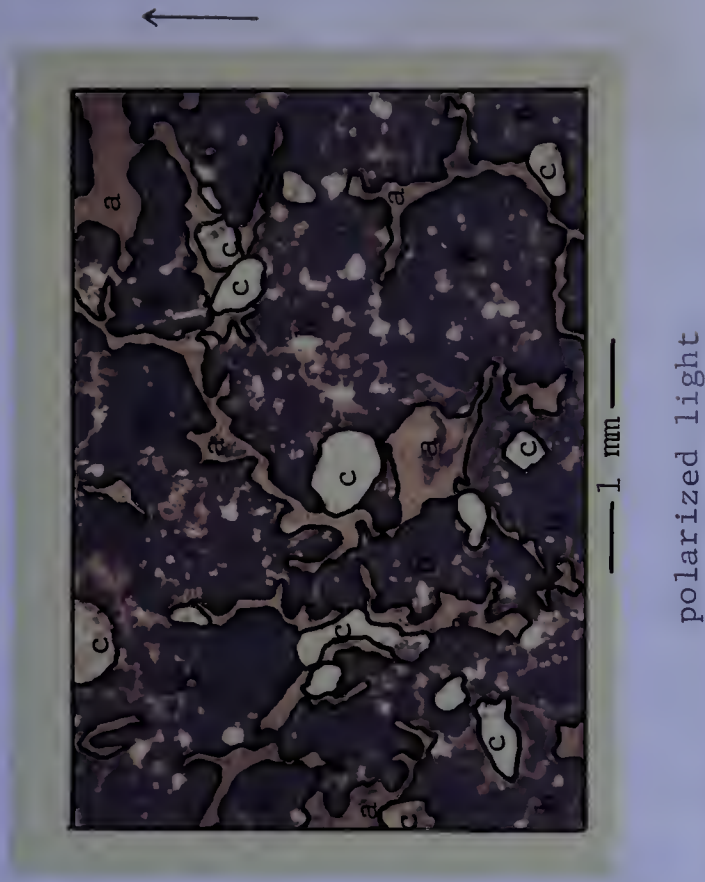
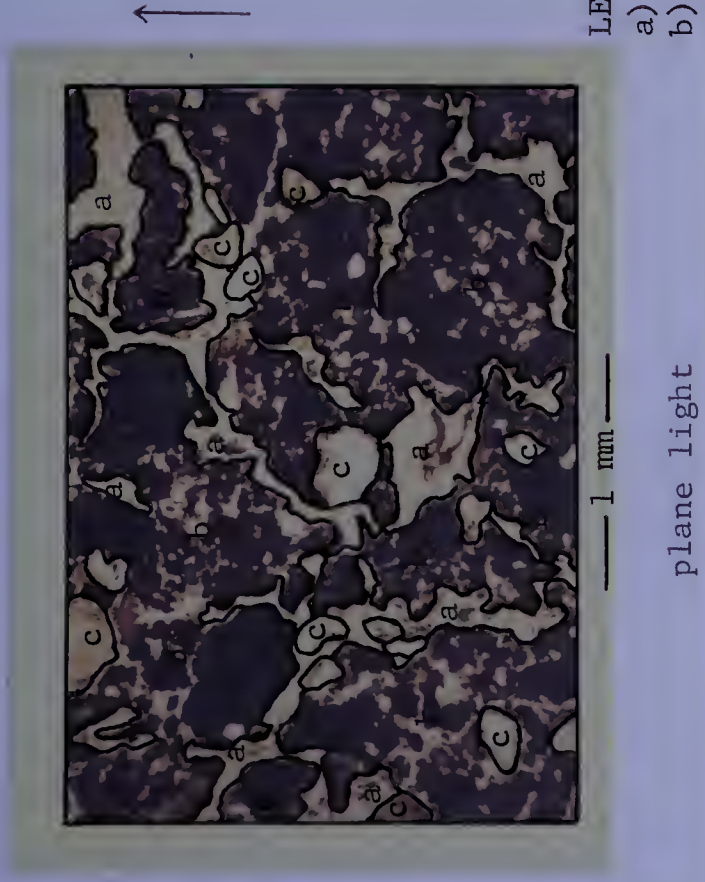


Plate 4. Photomicrographs of the Ah₂ horizon from the Olds sampling area.

Description of Plate 4

The photomicrographs comprising Plate 4 are typical of those taken of the Ah₂ horizon from the soil in the Olds sampling area. There is almost complete inclusion of skeletal grains by the plasmic material. Distinct granules have formed with approximate diameters of 0.5 mm to 1 mm or greater. The granules appear quite dense having a low percentage of inped voids. The lower two photographs illustrate the complete union of organic and inorganic materials. In addition, the lower two photographs illustrate "macro-bridging". The fabric of this Ah₂ horizon is similar to Kubiena's chernozemic fabric but tending toward intertextic fabric in which the skeleton grains are linked by intergranular braces or are embedded in a porous groundmass (Brewer, 1964).



LEGEND

- a). voids
- b). matrix
- c). large minerals

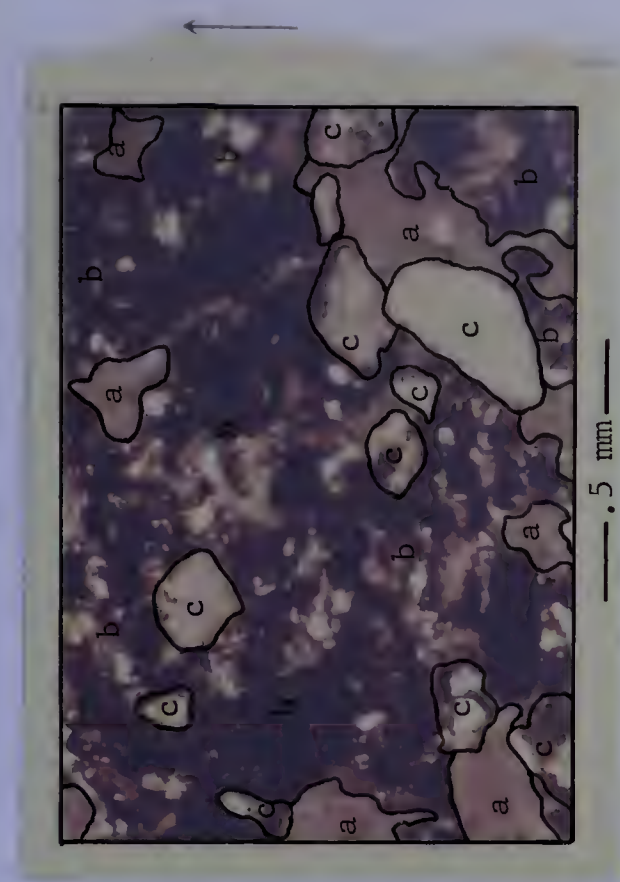
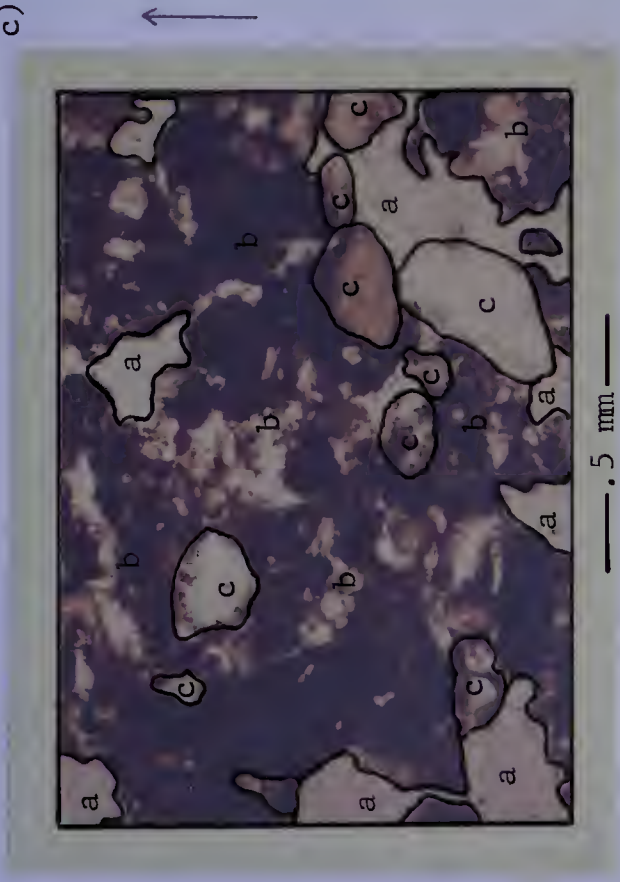


Plate 5. Photomicrographs of the Ah₁ horizon from the Edmonton sampling area.

— 2 mm —



— 2 mm —

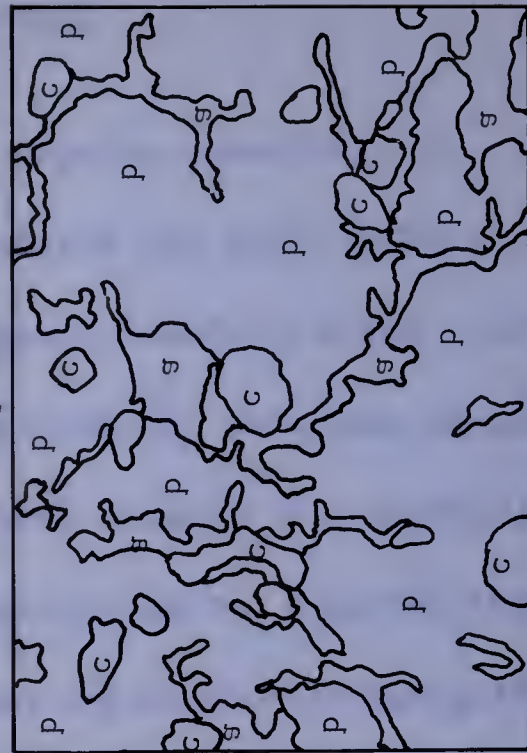


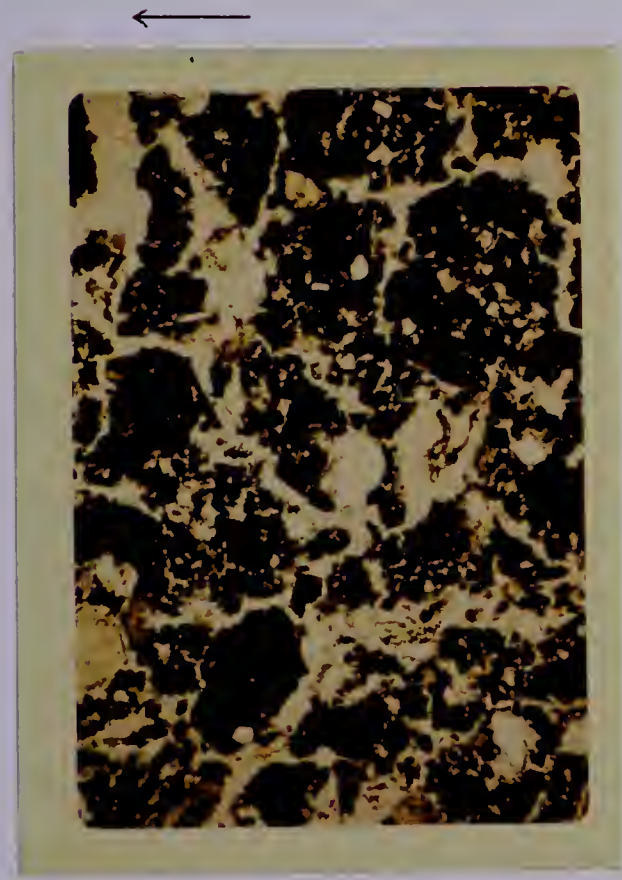
c). large minerals
p). matrix
s). voids
LEGEND

— 1 mm —



— 1 mm —





plane light



polarized light

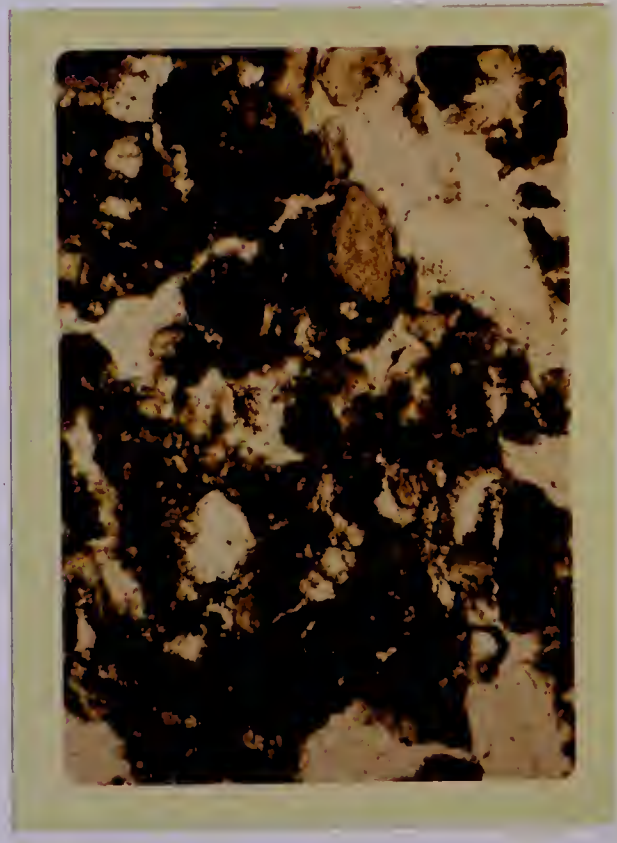
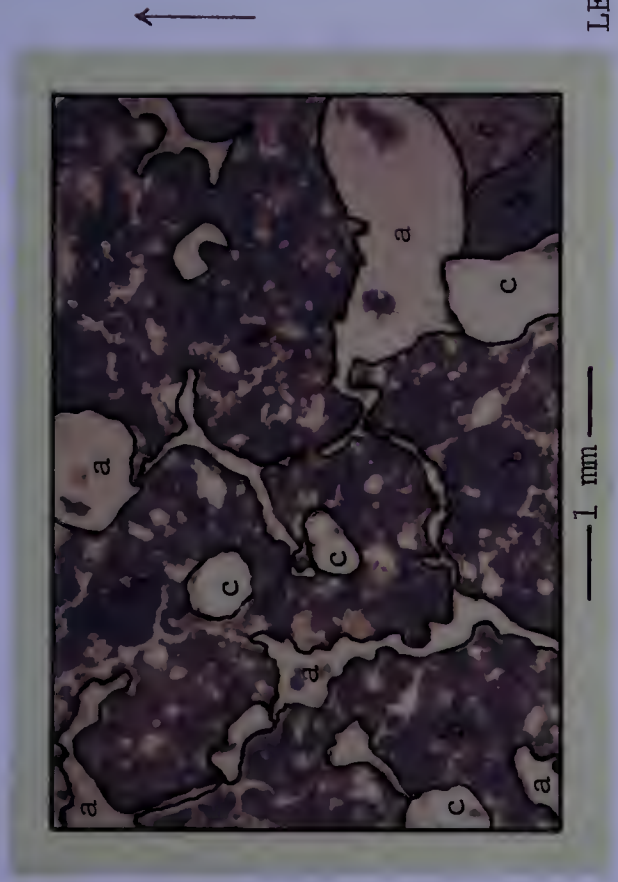


Plate 5. Photomicrographs of the Ah₁ horizon from the Edmonton sampling area.

Description of Plate 5

Plate 5 includes photomicrographs of the Ah₁ horizon from the soil in the Edmonton sampling area. The important features are the very dark color of the plasmic material as well as the intimate association of plasma and mineral grains. The large mineral grains when not incorporated into the plasmic material are thinly coated with organic material. A variety of granule sizes can be observed ranging in diameter from 0.2 mm to 0.8 mm or larger having irregular shape. The fabric is chernozemic tending toward intertextic.

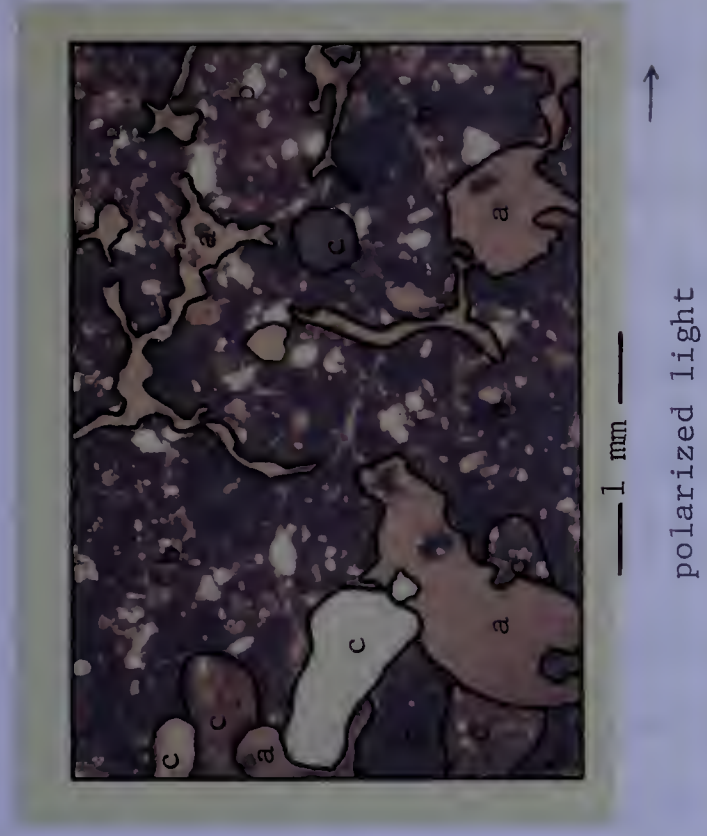


plane light

— 1 mm —

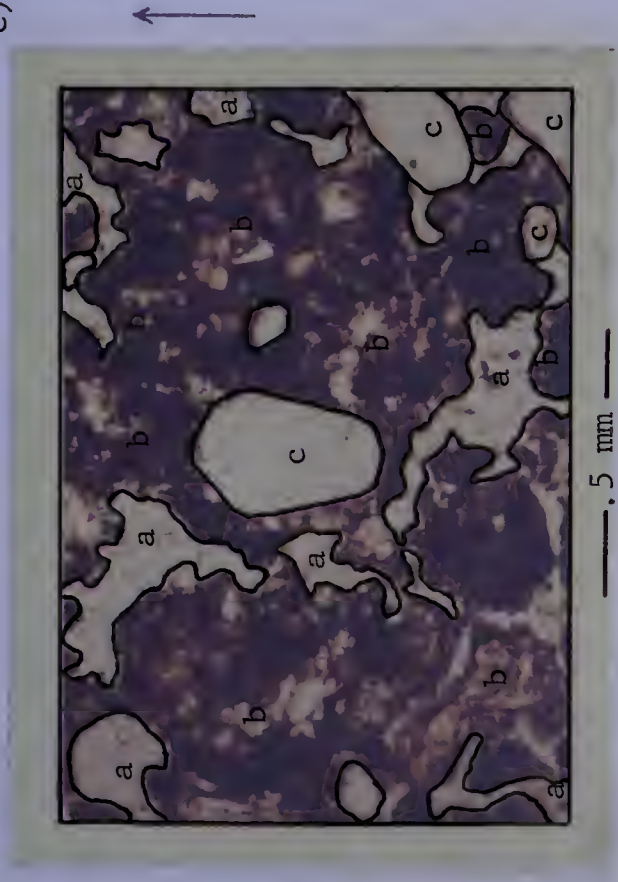
LEGEND

- a). voids
- b). matrix
- c). large minerals

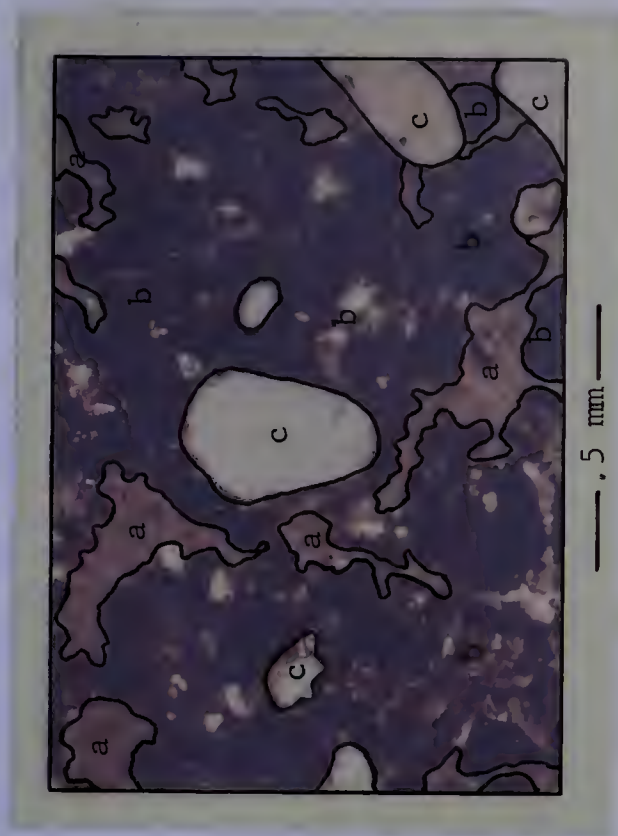


polarized light

— 1 mm —

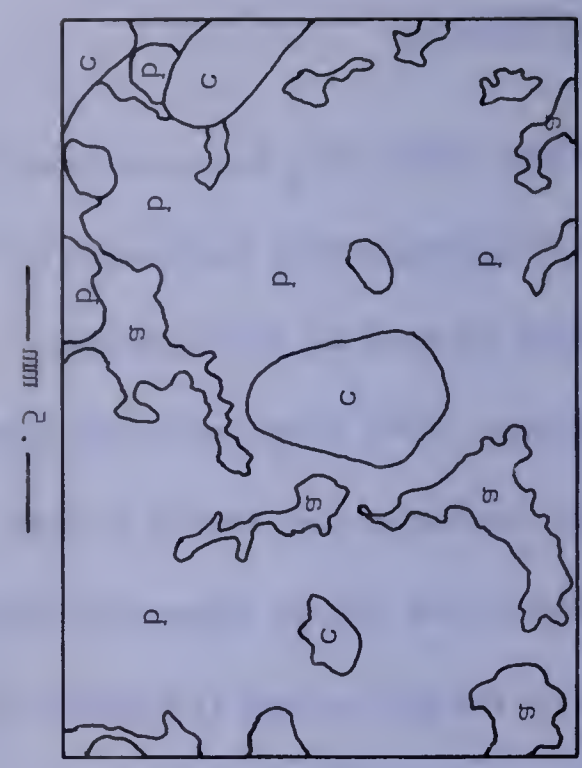


— 0.5 mm —

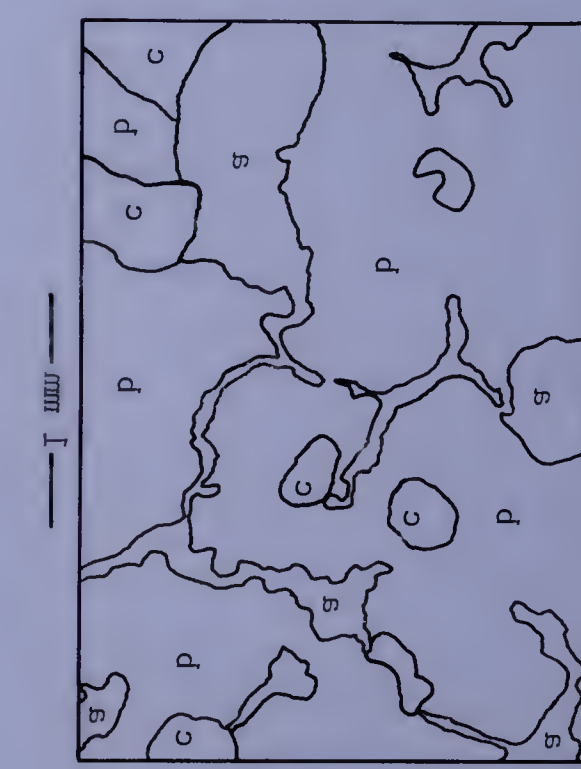
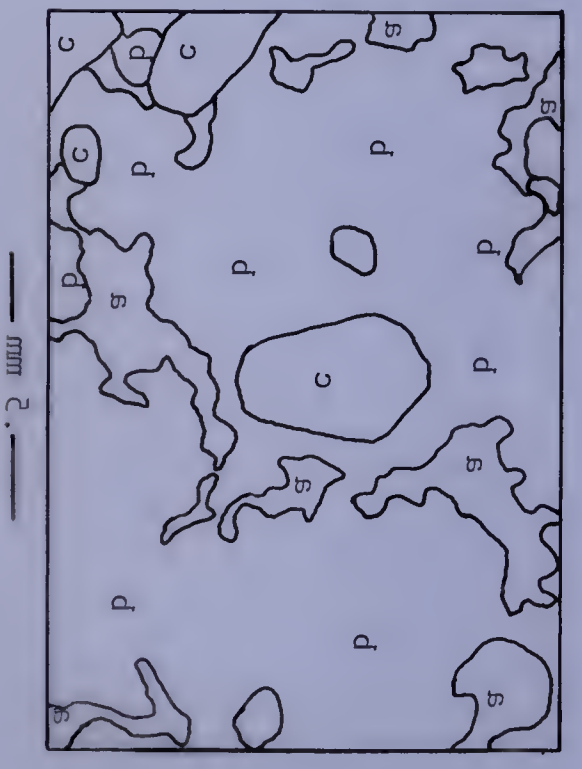


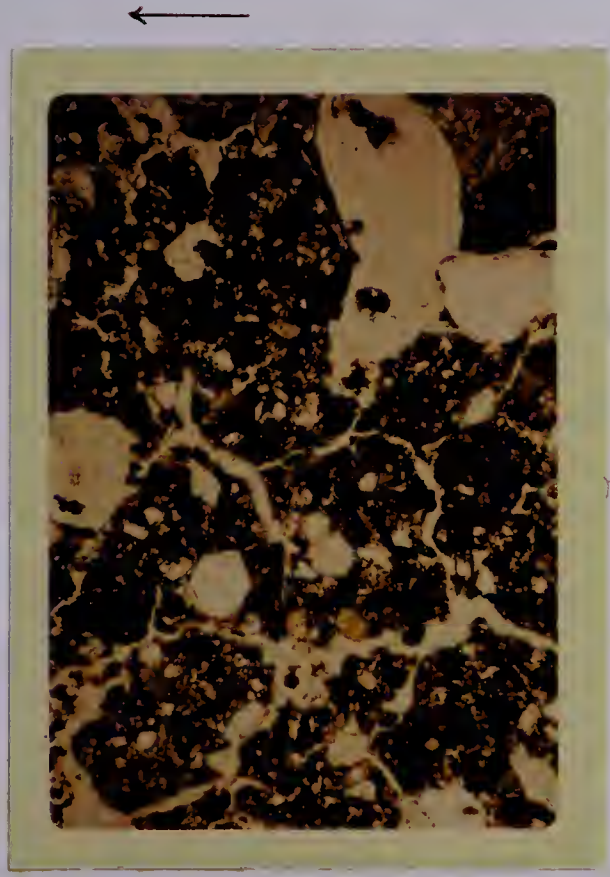
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Plate 6. Photomicrographs of the Ah₂ horizon from the Edmonton sampling area.

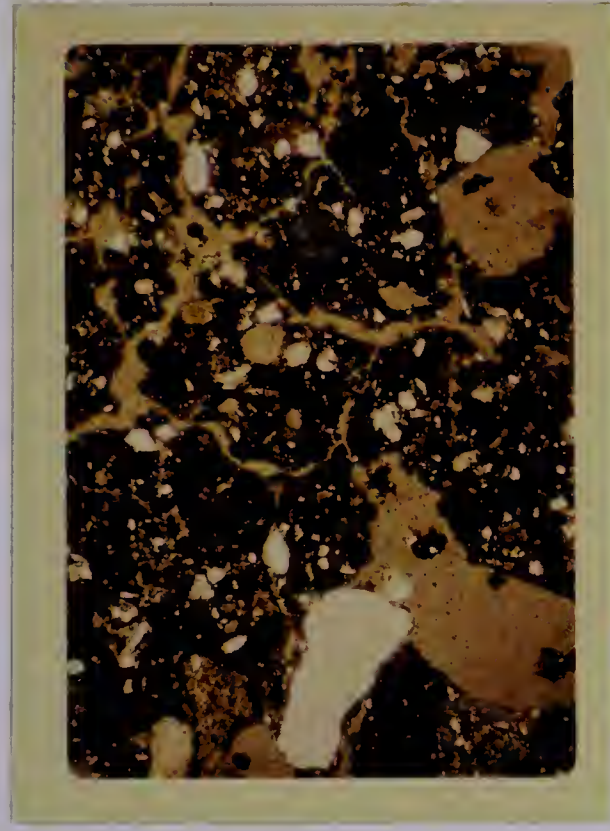


c). large minerals
 p). matrix
 s). voids
 LEGEND





plane light



polarized light

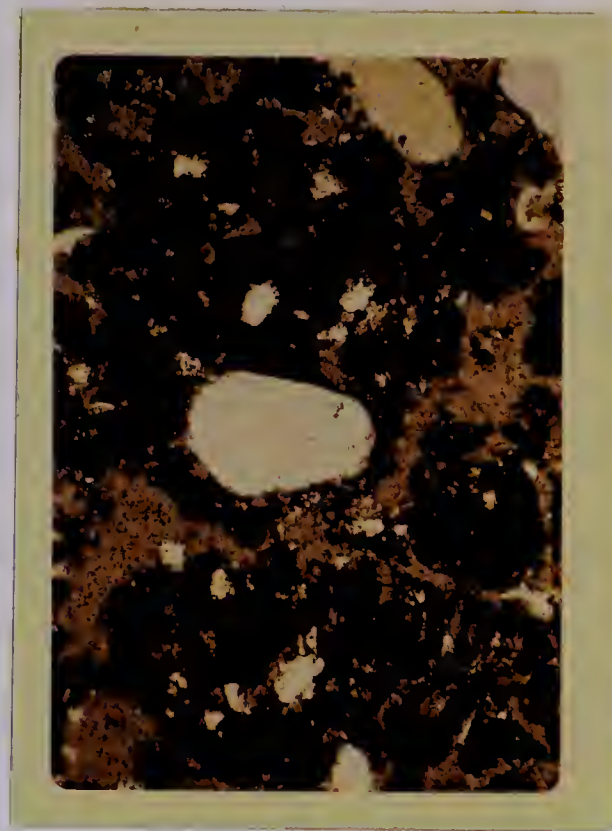
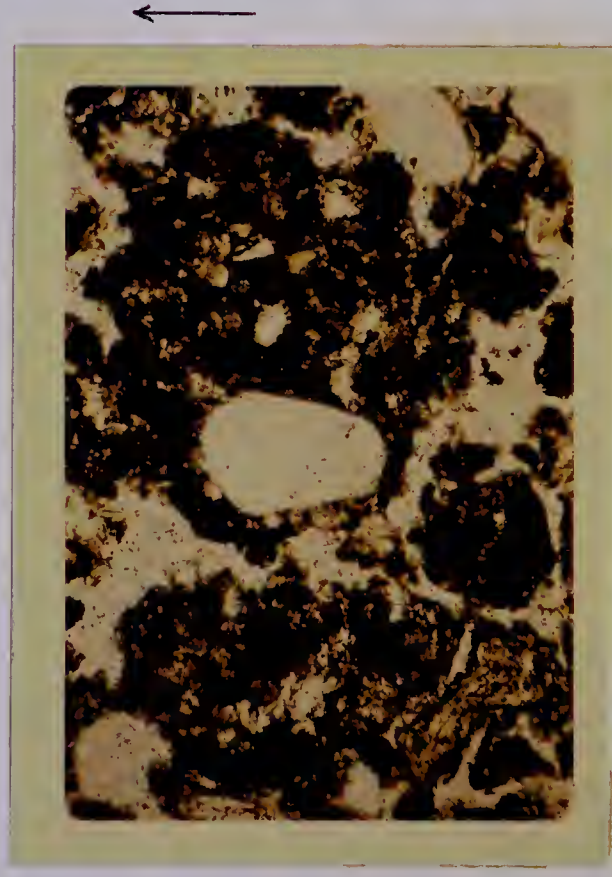


Plate 6. Photomicrographs of the Ah₂ horizon from the Edmonton sampling area.

Description of Plate 6

Features of the Ah₂ horizon from the Edmonton sampling area are illustrated in Plate 6. Plasmic and skeletal grains are united forming an intimate association of organic and inorganic soil constituents. The plasmic material is dark brown in color forming thin organic coatings on exposed edges of large mineral grains. Under low power magnification, irregular shaped granules varying in size from 0.25 mm to 1.0 mm and larger were observed. No preferred orientation of plasmic or skeletal grains was observed. According to Kubiena (1938) and Brewer (1964), the fabric is chernozemic but tending toward intertextic.

Close examination of the thin sections shows that plasmic material in the Ah₂ horizons is lighter in color than in the Ah₁ horizons. In addition, the matrix of the Ah₂ horizons appears denser than the matrix in the Ah₁ horizons. These trends were observed for all soils studied.

Organic Matter Analysis

Quantitative determination of polysaccharides and polyuronides.

Although several methods of extraction and hydrolysis of soil carbohydrates have been suggested, the method of Brink et al. (1960) was used for the hydrolysis and extraction of polysaccharides and polyuronides. The results obtained for hexose and pentose content by hydrolyzing with various normalities of H₂SO₄ are presented in Figure 4. On the basis of analyses of two different soils it was found that maximum amounts of hexose and pentose were obtained with the use of 2 N H₂SO₄. In addition, complete recovery of added dextrose was obtained only when 2 N H₂SO₄ was used for hydrolysis. Consideration of these results lead to the use of 2 N H₂SO₄ for hydrolysis of soil samples instead of 3 N or N H₂SO₄ as suggested by Brink (1960) and Cheshire (1966).

The hexose, pentose and polyuronide content of Ah horizons from each of the sites for the three major sampling areas are shown in Figures 5, 6 and 7. The hexose and pentose contents for the B horizons are illustrated in Figures 8 and 9. Statistical analysis of

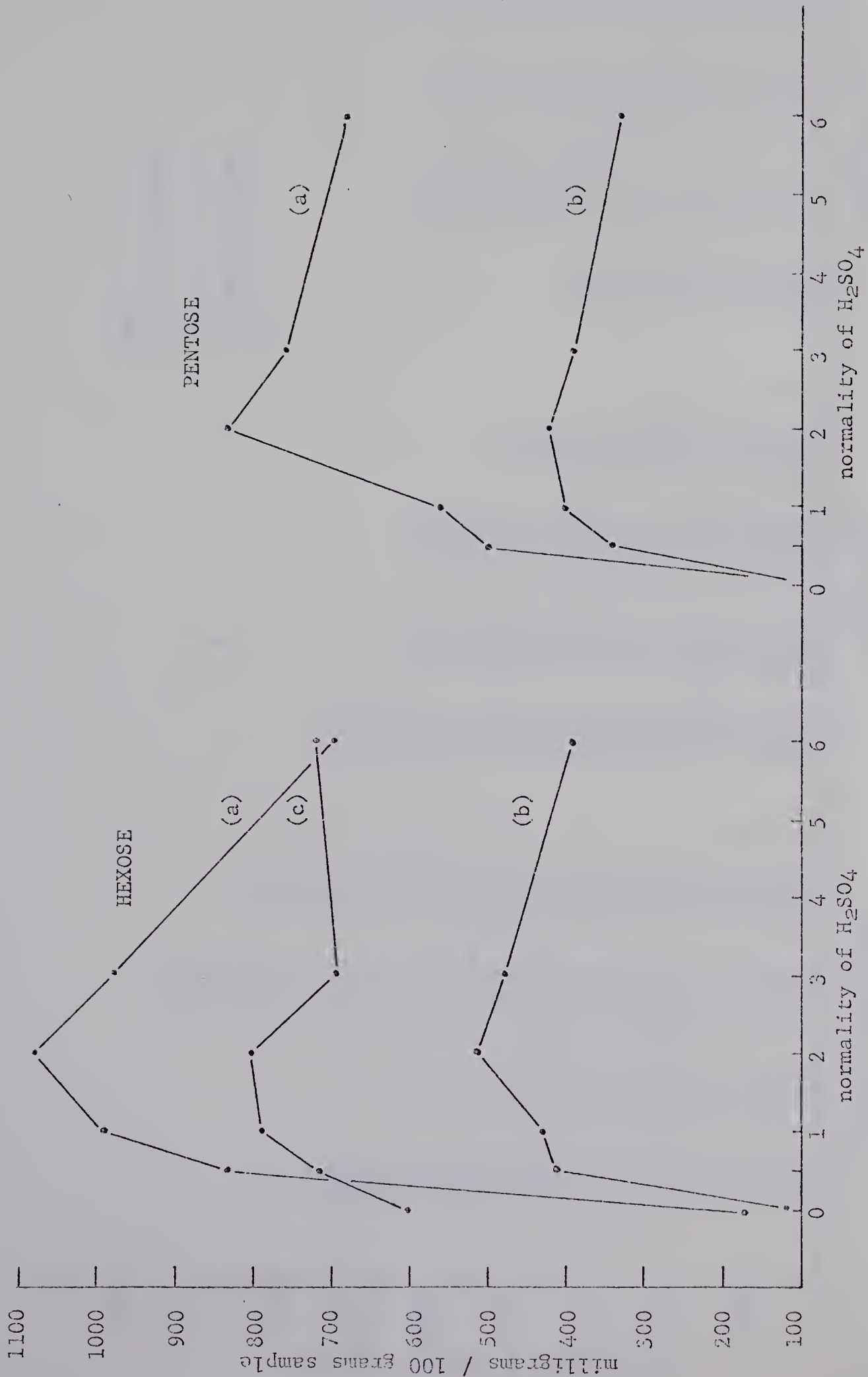


Figure 4 Effect of acid concentration used for hydrolysis on the extraction of hexose and pentose from:
 (a). soil from Ah₂ horizon - Pincher Creek area
 (b). soil from Ah₂ horizon - Edmonton area
 (c). 100 grams cleaned sand + 800 mgm dextrose

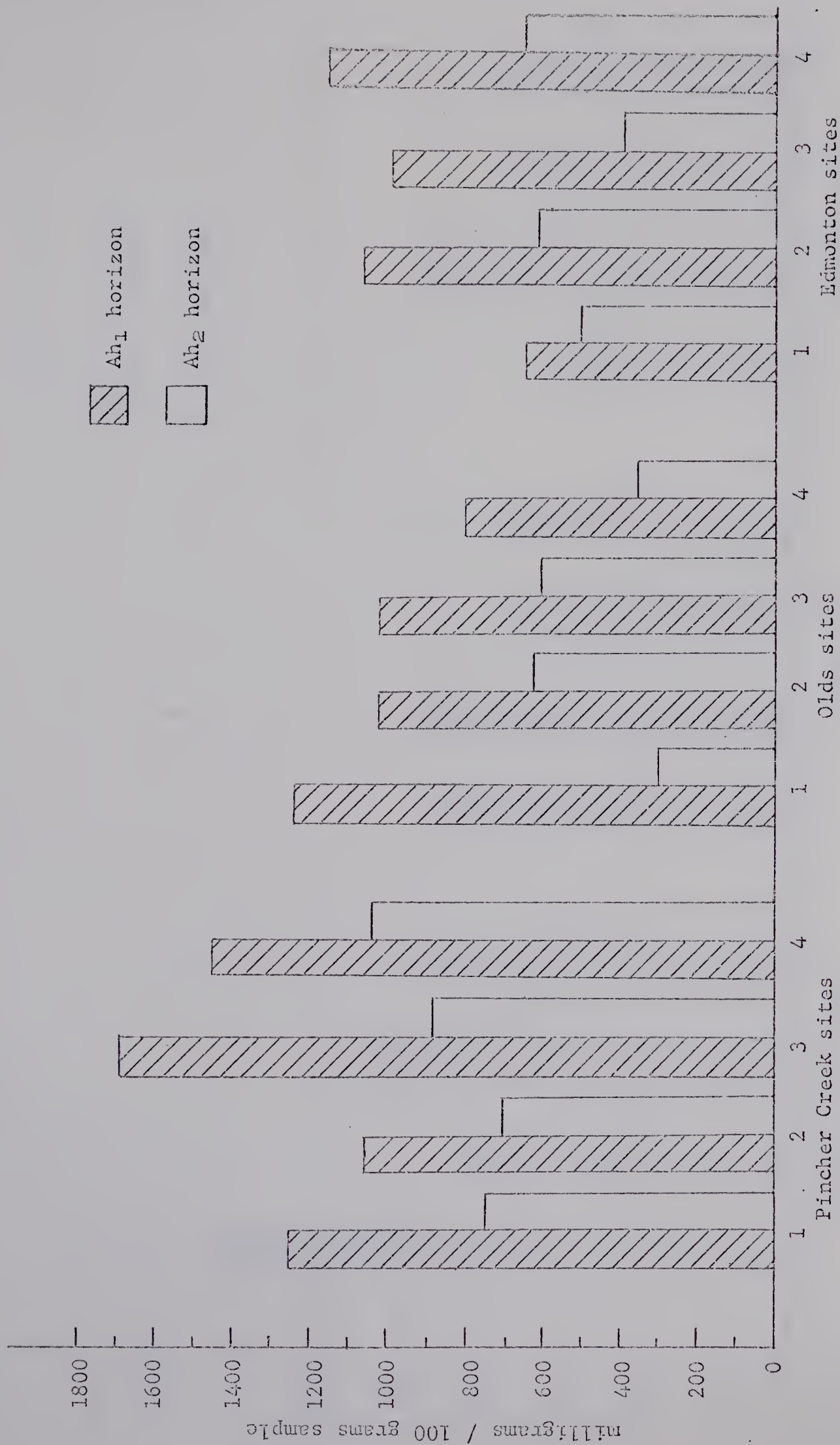


Figure 5 Hexose content of Ah horizons

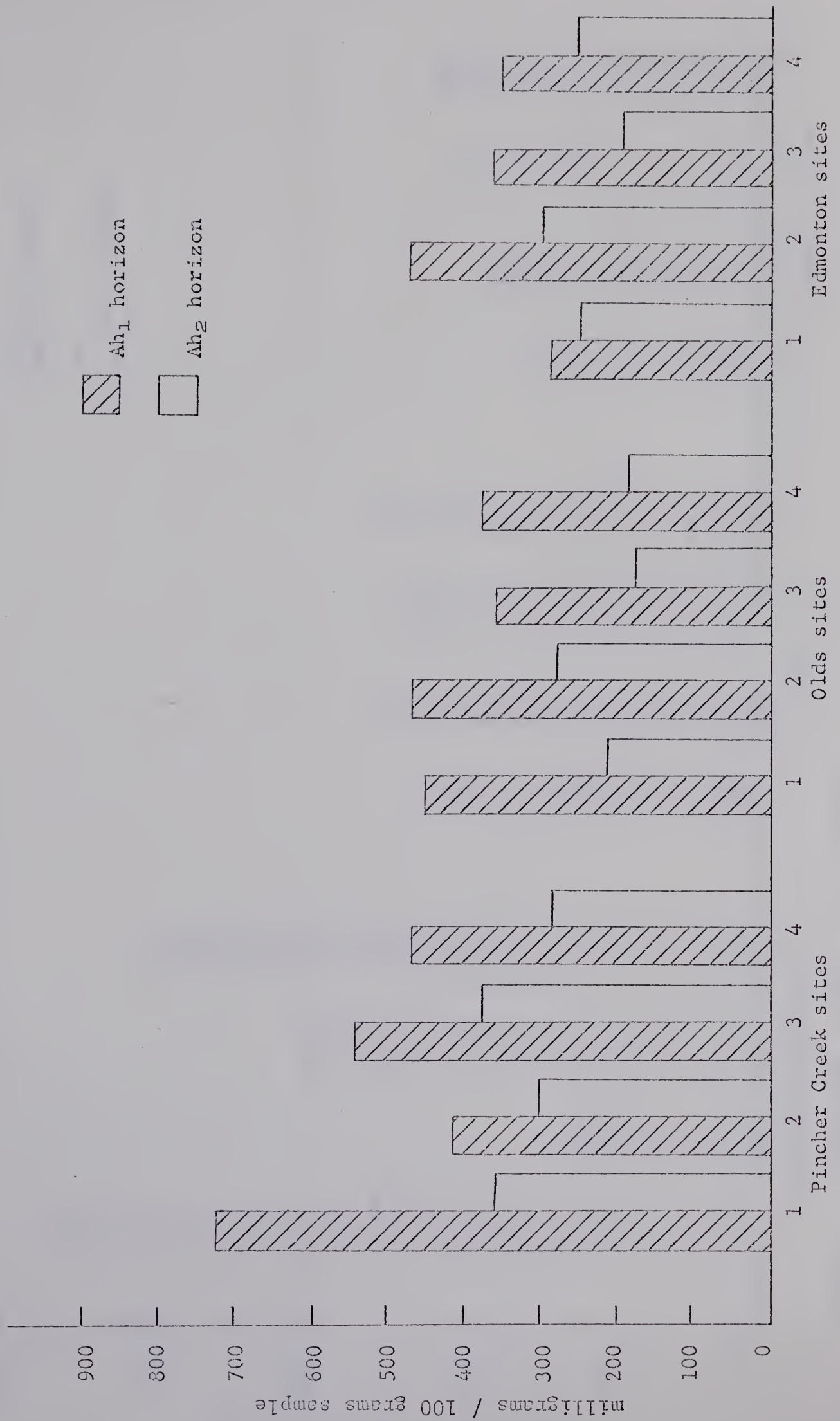


Figure 6 Pentose content of Ah horizons

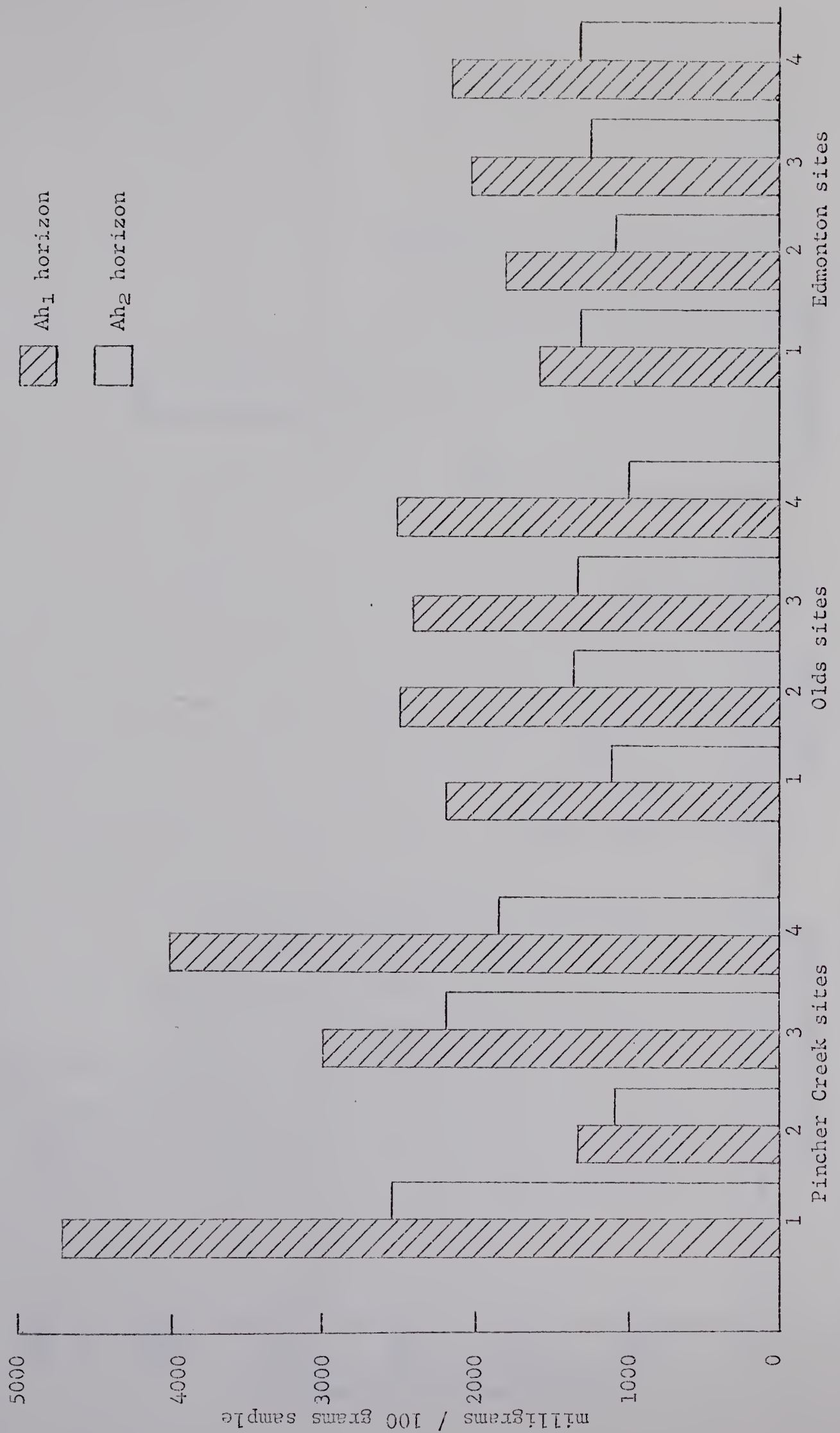


Figure 7 Polyuronide content of Ah horizons

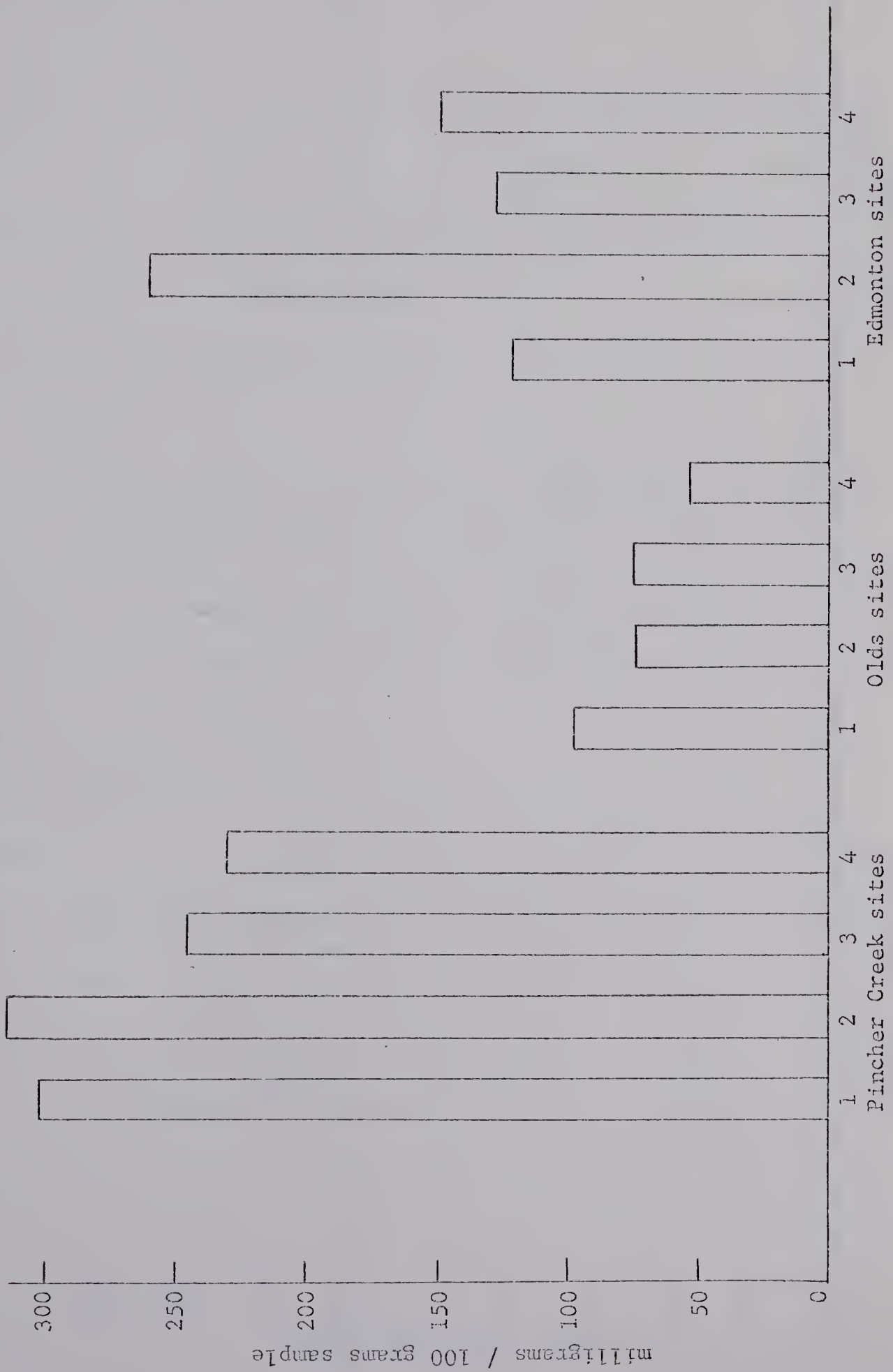


Figure 8 Hexose content of Bm horizons

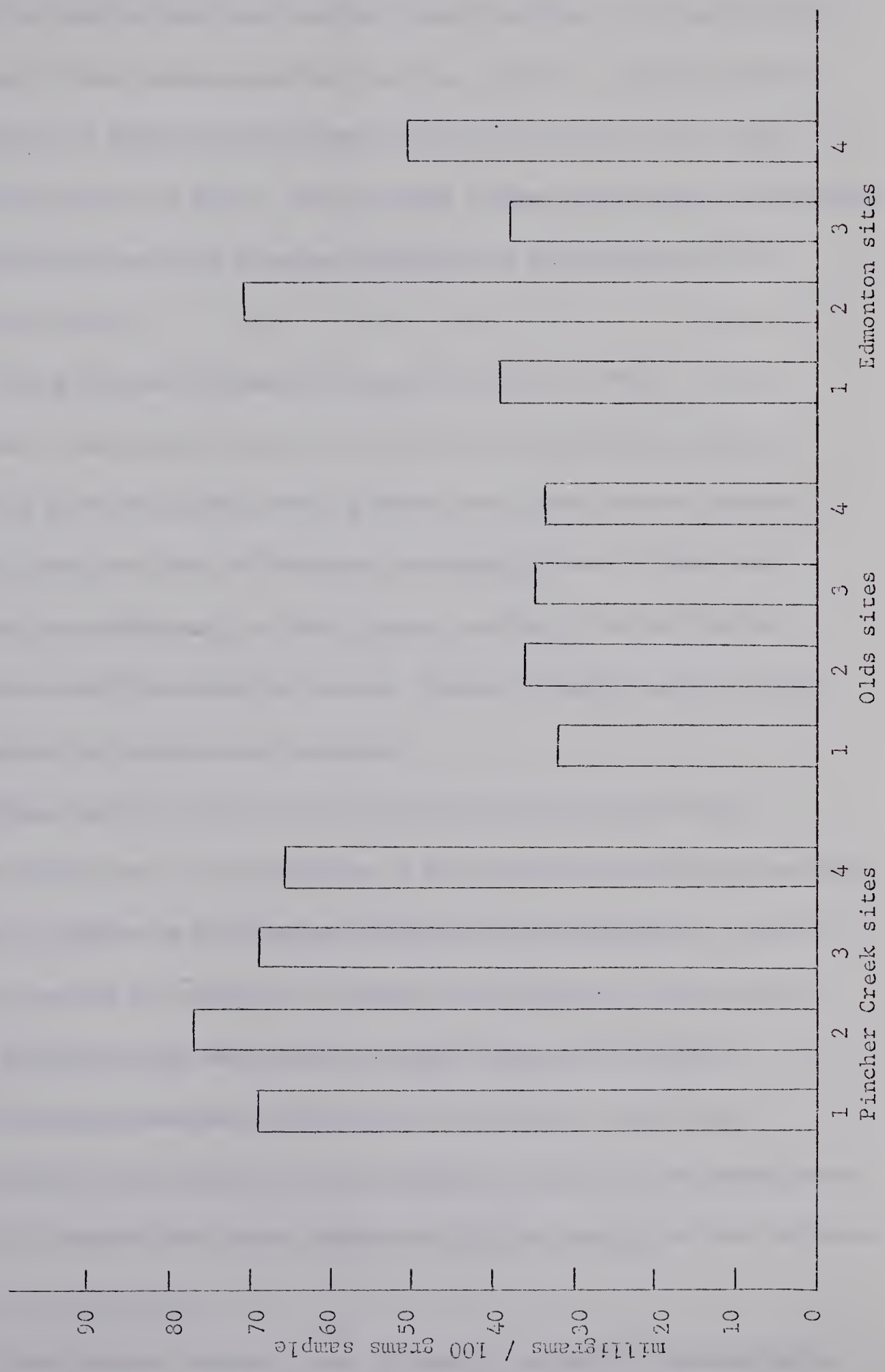


Figure 9 Pentose content of Bm horizons

the data in Figures 5 to 9 was conducted by using a simple factorial design for each of the three carbohydrate fractions. By analysis of variance, it was determined that hexose, pentose, and polyuronide contents were significantly higher in the Ah₁ horizons than in the Ah₂ horizons for all sites. Polyuronide content could not be determined for B horizons because of color interference resulting from the presence of iron.

Using Duncan's Multiple Range Test (Steel, 1960), it was found that total hexose content* of soil from the Pincher Creek sampling area was significantly greater than total hexose content in soils from the Olds or Edmonton sampling areas. There was no significant difference in total hexose content in soils from the Edmonton and Olds sampling areas. Similar results were obtained for pentose and polyuronide content.

When based on total soil polysaccharide and polyuronide content measured, an examination of the data revealed the polyuronide content is highest in all horizons within each sampling area. The pentose content was found to be lowest in all horizons within each major sampling area with hexose content being intermediate.

Although quantitative differences in hexose, pentose and polyuronides were shown to exist among horizons and sampling areas, it was not certain that these differences did not simply reflect different

* Total hexose content = sum of hexose content in Ah₁ horizons, Ah₂ horizons, and B horizons within one sampling area.

quantitative amounts of total organic matter. Therefore, polysaccharide carbon content was recalculated as per cent of total carbon content for each horizon.

Total carbon content in the Ah₁, Ah₂ and B horizons is given in Table IV. Since no CaCO₃ was detected in these horizons, it was assumed total carbon represented organic carbon. Using these values, the per cent of total carbon as hexose, pentose and uronic acid carbon was calculated and presented in Table V.

The average per cent of total carbon as polysaccharide and polyuronide carbon for all sites was 18.5% and 19.6% for the Ah₁ and Ah₂ horizons respectively for the Edmonton sampling areas. In the Olds sampling area the averages were 19.1% and 20.1% for the Ah₁ and Ah₂ horizons respectively. In comparison the per cent of total carbon as polysaccharide and polyuronide carbon for all sites in the Pincher Creek area was 26.6% and 27.6% for the Ah₁ and Ah₂ horizons respectively. These values are higher than those reported in the literature (Gupta, 1962). A possible explanation is that modification of Brink's method gave higher polysaccharide contents and the fact that most investigators do not determine pentose content in the soil polysaccharide fraction.

From statistical treatment (analysis of variance) of the data in Table V, it was found that pentose carbon as per cent of total carbon was significantly greater in the soils from the Pincher Creek sampling area than in the soils from the Olds or Edmonton sampling

TABLE IV. Total Carbon Content
(in per cent) of the Ah₁, Ah₂ and Bm Horizons

Sampling Area	Site no.	Soil Horizon		
		Ah ₁	Ah ₂	Bm
Edmonton	1	5.39	3.54	.84
	2	6.55	4.29	1.32
	3	6.98	3.27	.77
	4	6.64	4.01	.97
Olds	1	8.61	3.92	.61
	2	8.12	4.53	.61
	3	6.68	3.32	.54
	4	6.27	2.76	.52
Pincher Creek	1	9.71	5.12	1.33
	2	6.03	3.93	1.20
	3	7.42	5.14	1.07
	4	6.33	3.67	1.00

TABLE V. Pentose, Hexose and
Uronic Acid Carbon as per cent of Total Carbon

		Soil horizon								
Sampling area	Site no.	Ah ₁			Ah ₂			Bm (Btj)		
		1	2	3	1	2	3	1	2	
Edmonton	1	2.14	4.82	10.41	2.74	5.76	12.55	1.86	5.69	
	2	2.88	6.47	9.71	2.80	5.87	8.52	2.14	8.00	
	3	2.06	5.73	9.97	2.30	5.02	12.84	1.96	6.51	
	4	2.11	7.05	10.95	2.49	6.48	11.08	2.08	5.77	
Olds	1	2.12	5.76	8.76	2.12	3.06	9.88	2.15	5.92	
	2	2.30	5.02	10.54	2.30	5.47	10.05	2.39	4.65	
	3	2.16	6.11	12.28	2.12	11.57	13.71	2.62	5.44	
	4	2.40	5.23	13.65	2.55	5.22	12.31	2.54	4.12	
Pincher Creek	1	2.96	7.84	21.68	3.05	8.06	16.48	2.62	12.08	
	2	2.93	7.76	13.73	2.93	7.94	14.67	2.59	8.82	
	3	2.76	7.03	13.36	3.05	7.12	20.50	2.58	8.20	
	4	2.97	6.92	16.57	2.81	6.88	17.01	2.08	10.04	

1 - Pentose carbon

2 - Hexose carbon

3 - Uronic acid carbon

areas. The results for pentose carbon as per cent of total carbon in soils from the Olds sampling area do not differ significantly from the values reported for soils from the Edmonton sampling area. Similar results were obtained for hexose and polyuronide carbon contents. Applying Duncan's Multiple Range Test to horizons and pentose carbon content, it was found that Ah₁ and Ah₂ horizons do not differ significantly from each other in pentose carbon content when determined as per cent of total carbon. The B horizons were found to be significantly lower in pentose carbon content than the Ah₁ and Ah₂ horizons. Furthermore, there was no significant difference in hexose and polyuronide carbon content (expressed as per cent of total carbon) between horizons.

The results of this investigation indicate a larger proportion of the organic carbon in the soil from the Pincher Creek sampling area was in polysaccharide-polyuronide form than in soils from the Olds and Edmonton sampling areas. The proportion of total carbon as polysaccharide and polyuronide carbon remains constant with depth (except for pentose carbon where a decrease occurs in the B horizon). Graveland (1960) found a disproportionate relationship where an increase of sugar carbon to total carbon occurred with depth. Sawyer (1962), working with Dark Gray Wooded soil, found that the ratio of polyuronide and polysaccharide carbon to total organic carbon showed little change with depth. Dormaar (1967) reported similar results where the polysaccharide carbon expressed as

percentage of total carbon remained fairly constant between Ah and Bm horizons of Thin Black soils.

Although the results indicate quantitative differences in polysaccharide and polyuronide content among horizons and sampling areas, the interpretation of these results should be approached cautiously. The method of extraction of soil carbohydrates used in this study may have the limitation that only relatively free or uncombined soil carbohydrates were removed. In this regard, it is felt that the higher polysaccharide and polyuronide content found in the soils from the Pincher Creek sampling area may represent a higher relative content of free or uncomplexed carbohydrate material. This postulation is somewhat substantiated by the work of Graveland et al. (1961) where a 222 per cent increase in uronic acid was obtained by treating soil (Angus Ridge, Ah₂ horizon) with HF-HCl solutions. The authors suggested that, "because of the increased solubility of organic matter after HF-HCl treatments, an intimate association of clay minerals and soil carbohydrates occur". In view of Graveland's work it appears that differences in polysaccharide and polyuronide contents found to exist in this study are likely to be reflections of the degree of complexing of these materials rather than differences in total amounts.

It has been shown that a significant difference exists in the microstructure and carbohydrate content in soils from the Pincher Creek area as opposed to soils from the Edmonton and Olds sampling

areas. Although attempts have been made to correlate aggregate size and stability to polysaccharide and polyuronide content (Toogood et al., 1959; Greenland et al., 1962; Acton et al., 1963 and Salmon, 1963) it would seem of little benefit to attempt any such correlation in this investigation. It is recognized in this study that the values obtained for polysaccharide and polyuronide content by the conventional method (H_2SO_4 hydrolysis) are values more indicative of that part of the carbohydrate fraction not involved in aggregate formation (organo-clay complexes). In order to attempt a correlation between aggregate size and polysaccharide content it would be necessary to obtain information on the amount of complexed polysaccharides and polyuronides rather than free or total content.

Humic acid analysis. Three humic acid samples were obtained by pooling soil from Ah_2 horizons so that the four sites within each major sampling area constituted one sample. The functional group analysis of the extracted humic acids are outlined in Table VI. Total functional groups are highest for humic acids extracted from soils in the Olds area followed by the Pincher Creek area. Humic acid from the soil in the Edmonton sampling area was found to have the lowest content of total functional groups. Although values are based on ash free weights, the higher ash content for humic acid obtained from soil in the Edmonton area may account for some reduction in the exchange-absorption capacity. If the ash components are complexed to humic acid through COOH and OH groups, these groups would not

TABLE VI. Functional Group Analyses
of Humic Acid Separated from Pooled Ah₂ Horizons

Exchange-Absorption Capacity me. / 100 g Humic Acid					
Humic acid sample	Ash content %	Total* functional groups	COOH** groups	Phenolic*** OH groups	Titrat-able****H ⁺
Edmonton	3.95	624	439	185	486
Olds	2.69	887	462	425	497
Pincher Creek	1.41	745	405	340	437

* determined by barium acetate method

** determined by calcium acetate method

*** determined by difference (total functional groups - COOH groups)

**** determined by titration of Na-humate with HCl to pH 7.0

participate in exchange reactions, consequently lowering the total exchange-absorption capacity. Pincher Creek humic acid, having the lowest ash content, would suggest least organo-mineral complexing in soils from this area as compared to soil in the Olds and Edmonton areas.

The infrared spectra of the humic acid samples are presented in Figure 10 and show good agreement with the analytical data (Table VI). The broad absorption band with a maximum at 3380 cm^{-1} has been attributed to hydrogen bonded hydroxyls. Absorption bands in the 2920 cm^{-1} and 2850 cm^{-1} regions have been attributed to aliphatic C-H groups. Other main groups revealed by infrared analysis are C=O frequency of COOH, C=O stretch of ketonic carbonyl (1725 cm^{-1}); quinone carbonyl groups (1660 cm^{-1}); C=C of aromatic rings (1610 cm^{-1}); CH_3 and CH_2 aliphatic groups (1375 cm^{-1}) and C-O stretching or bending vibrations of OH groups (1207 cm^{-1} and 1010 cm^{-1}) (Then, 1966; Kononova, 1966; Schnitzer, 1964, and Wagner, 1965).

Comparison of the absorption band at 1730 cm^{-1} for the three humic acid samples reveals an increase in intensity in the order Olds > Edmonton > Pincher Creek. The 1730 cm^{-1} absorption band has been attributed to C=O frequency of COOH groups. The relative increase in intensity of the 1730 cm^{-1} absorption band agrees with the analytical data for the exchange-absorption capacity (Table VI) resulting from the presence of COOH groups. The analytical data indicate phenolic OH groups are highest in the Olds humic acid sample;

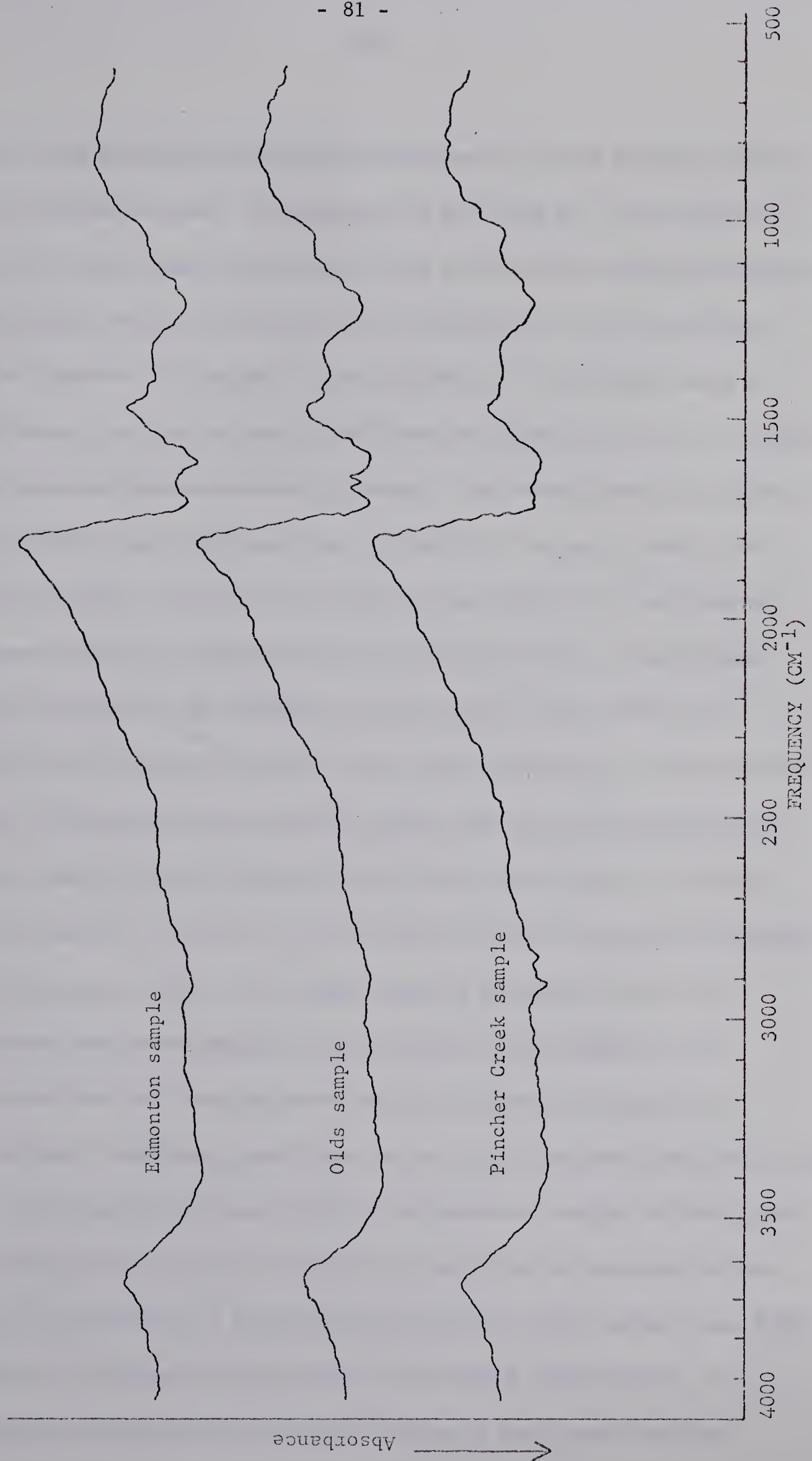


Figure 10 Infrared spectra of humic acid separated from the pooled Ah₂ horizons

lowest in the Edmonton sample with the Pincher Creek sample having an intermediate content. Examination of the 1210 cm^{-1} and 1010 cm^{-1} absorption bands which have in part been attributed to bending vibrations of OH groups reveals reasonably good correlation with the analytical data for phenolic OH content. A weak 1660 cm^{-1} absorption band in the infrared spectrum of humic acid from the Olds Ah₂ horizons suggests the presence of quinone carbonyl groups. The broad hydrogen bonded OH absorption band with maximum at 3400 cm^{-1} appears similar for all three samples. The C=C absorption band (1610 cm^{-1}) attributed to aromatic rings is relatively lower in intensity with a concomitant relative increase in the aliphatic C-H absorption band (2850 cm^{-1} and 2920 cm^{-1}) for the Pincher Creek humic acid sample. This would suggest a decrease in the aromatic nature with an increase towards an aliphatic nature for the Pincher Creek humic acid sample. As humic acids increase in "maturity" their aromatic nature becomes increasingly clear (Kononova, 1966). The slight relative decrease in the C=C absorption band accompanied by an increase in the aliphatic C-H absorption band for Pincher Creek humic acid would suggest it is less "mature" than humic acid from soils in the Edmonton and Olds areas.

According to Dormaar (1967), the molecular weight of humic and fulvic acid can be related to the slope of the infrared spectrum in the 2500 cm^{-1} to 1800 cm^{-1} region where a positive slope (going from 2500 to 1800 cm^{-1}) indicates large molecular weights (humic acid). A flattening of the slope, and a negative slope is associated with low

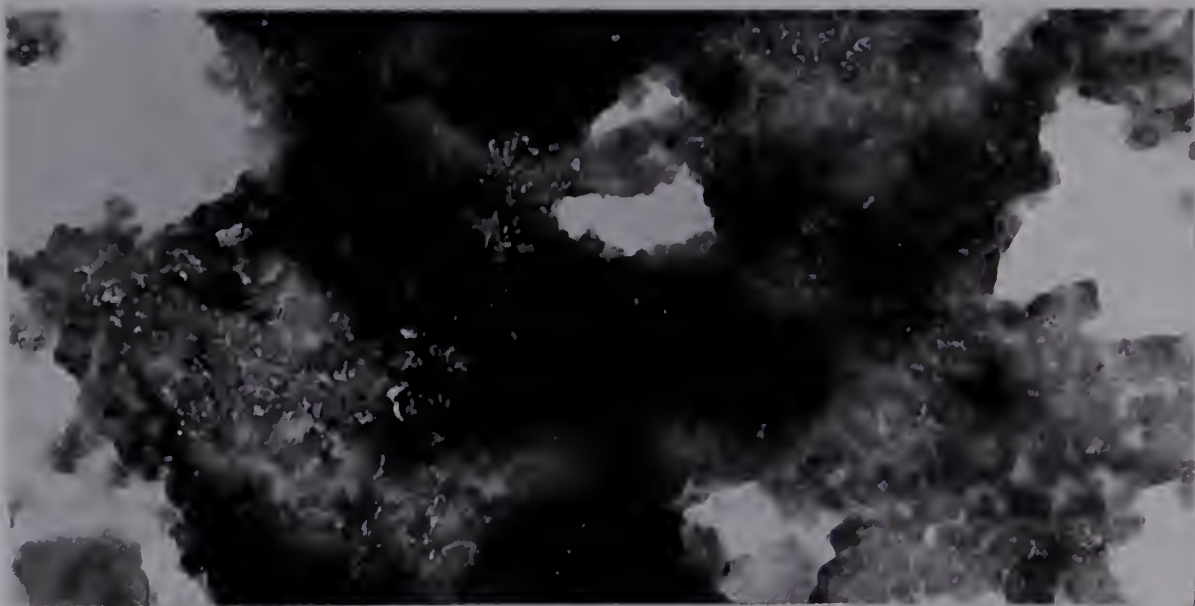
molecular weights (fulvic acid). Examination of the infrared spectra in Figure 10 reveals positive slopes occurring in the $2500 - 1800 \text{ cm}^{-1}$ region which are characteristic for humic acid developed under grass vegetation (Dormaer, 1967). The slope of the infrared spectrum in the 2500 to 1800 cm^{-1} region for the Pincher Creek humic acid sample appears slightly flatter and indicates a slightly lower molecule weight.

The general features of the infrared spectra for the three humic acid samples are in agreement with reported results (Kononova, 1966; Dormaar, 1967 and Sawyer, 1962) for humic acid of similar origin. Since the extraction method used for humic acid removal is selective in that only loosely bound or free organic matter is removed, it is not expected that great differences should arise in the exchange-absorption capacity and infrared spectra among the three humic acid samples.

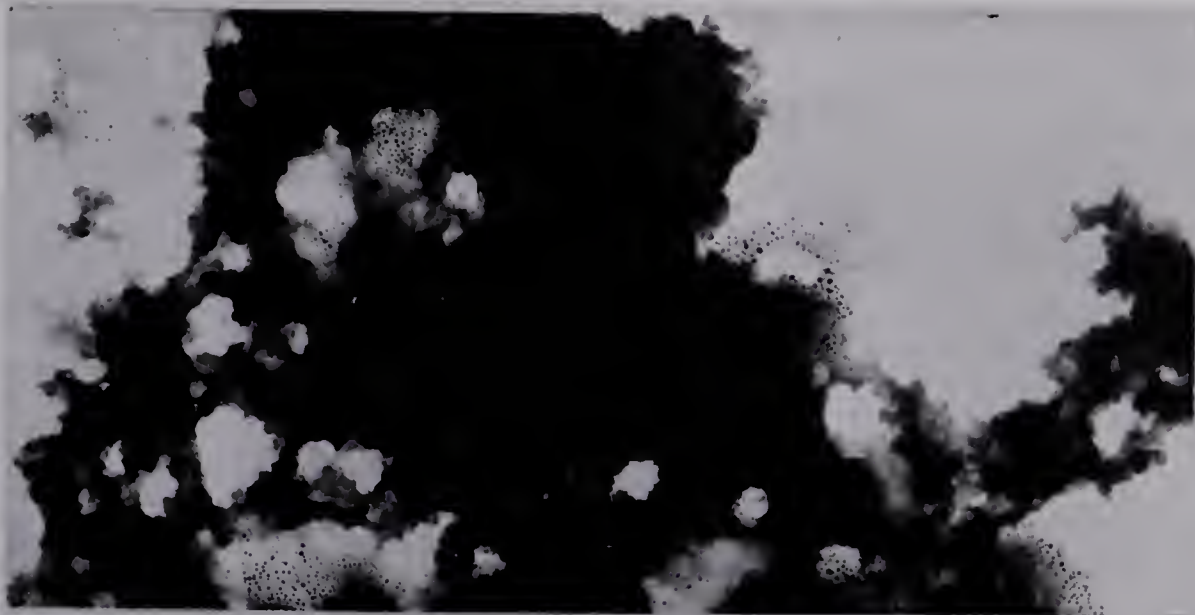
Electron micrographs of the three humic acid samples are presented in Plate 7. Humic acid has been described as consisting of tiny spherical particles uniting into chains and aggregates and having a loose spongy structure (Kononova, 1966). The morphological appearance of humic acid from the soils in the Edmonton (photograph 2) and Pincher Creek (photograph 3) areas fit this description well. The dense appearance of the humic acid from the soils in the Olds area (photograph 1) is felt to be due to a slight peptization of the humic acid caused by an increase in pH during dialysis rather than due to a chemical difference. Photograph 1 of Plate 8 is an electron micrograph of low molecular weight fulvic acid. Considering the difference in magnification, it has a similar appearance to humic acid.



1



2



3

Plate 7 Electron micrographs of humic acid separated from the Ah₂ horizon from the 3 major sampling areas.

Description of Plate 7

Photograph 1. Electron micrograph of humic acid obtained from the pooled Olds sites - Ah₂ horizon.

Photograph 2. Electron micrograph of humic acid obtained from the pooled Edmonton sites - Ah₂ horizon.

Photograph 3. Electron micrograph of humic acid obtained from the pooled Pincher Creek sites - Ah₂ horizon.

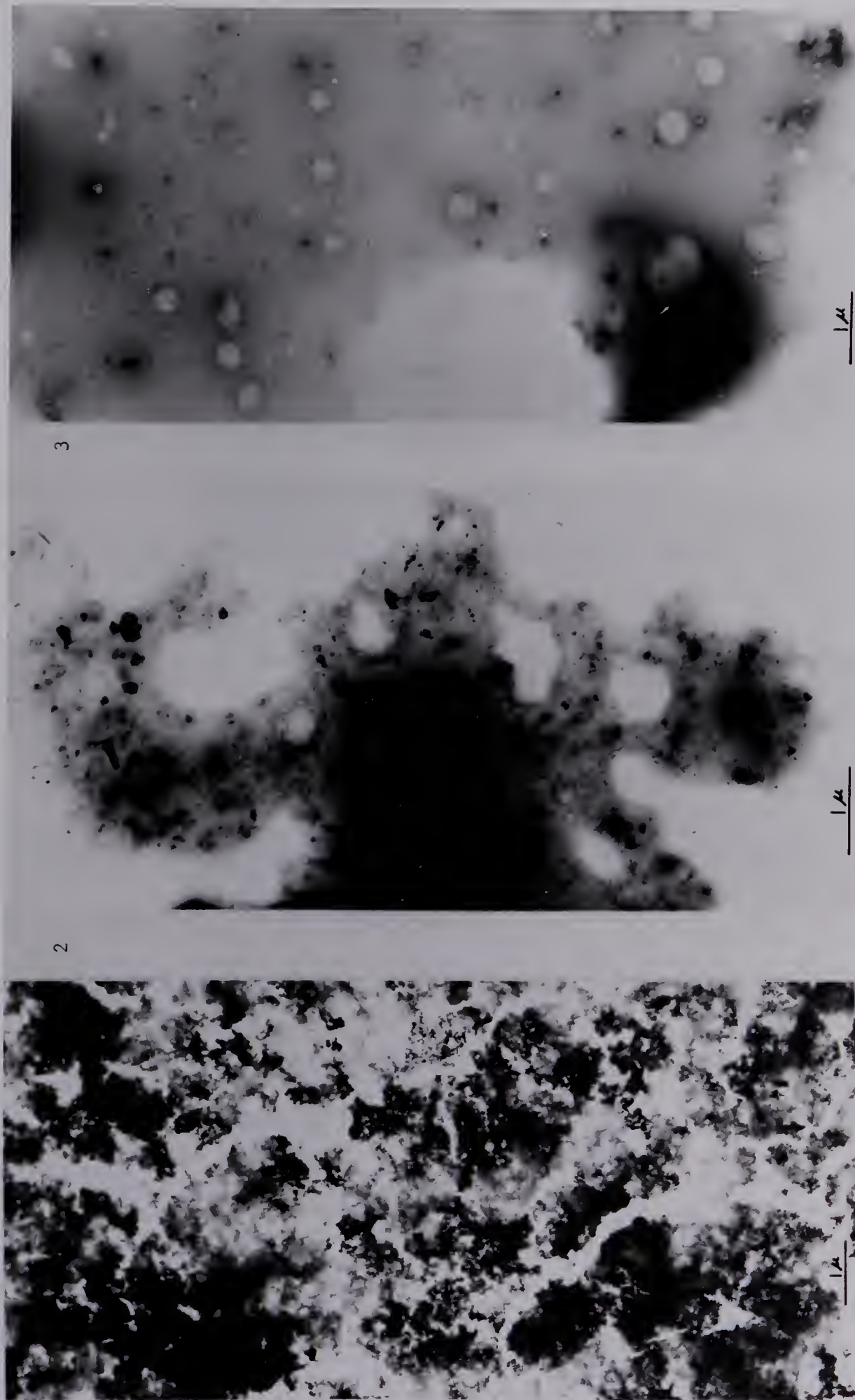


Plate 8 Electron micrographs of soil organic matter separated from the Ah₂ horizon-Pincher Creek area.

Description of Plate 8

Photograph 1. Electron micrograph of organic matter extracted with hot 2 N H_2SO_4 from an Ah_2 horizon in the Pincher Creek sampling area. Before photographing the pH of the extract was raised until the organic material precipitated. This was followed by one week of dialyzing. Obtained in this manner, it can be considered as the fulvic acid fraction.

Photograph 2. Electron micrograph of hot water soluble organic matter extracted from an Ah_2 horizon located in the Pincher Creek sampling area. Before photographing, this fraction was concentrated by vacuum evaporation.

Photograph 3. Electron micrograph of hot water soluble organic matter extracted from an Ah_2 horizon located in the Pincher Creek sampling area.

Clay Mineralogical Analysis of B and C Horizons

Semi-quantitative estimations of clay minerals in the total clay fraction of B and C horizons were made using X-ray diffraction data as well as chemical and physical analysis.

X-ray diffraction patterns of total clay from the C horizons are included in Figures 11 to 13. Table Ia in the appendix was included for the conversion of degrees 2θ to d-spacing in angstrom units. Physical and chemical analysis of these clays together with estimations of their relative amounts are presented in Table VII.

Estimates of the amounts of illite and montmorillonite present in the total clay fraction separated from C horizons were calculated on the basis of K_2O content, cation exchange capacities, and surface area determinations. The illite content was determined by assigning all the potassium to illite and assuming illite to have a K_2O content of 10 per cent (Mehra, 1959). Once the amount of illite present had been calculated and by assigning to it a cation exchange capacity of 20 me./100 g and a surface area of $10\text{ m}^2/\text{g}$, it was possible to estimate the amount of montmorillonite on the basis of the remaining portions of the exchange capacity and surface areas. A cation exchange capacity of 89 me./100 g and a total surface area of $980\text{ m}^2/\text{g}$ were assigned to montmorillonite thereby making it possible to calculate the montmorillonite content of the clays by two methods. The relative amounts of kaolinite, chlorite and quartz were based on examination of X-ray diffractograms.

In general, the clay fraction of the C horizons is predominantly montmorillonite and illite. Lesser amounts of chlorite, kaolinite and quartz were found in these horizons. There is good agreement between calculated values for montmorillonite and illite and X-ray diffraction patterns. From the data presented in Table VII the clay fractions from the C horizons were found to be very similar with the exception of site 3 and 4 in the Olds area. In these sites it was found that the montmorillonite content was lower with a concomitant increase in chlorite content.

The presence of interstratified clay minerals in the C horizon clays is suggested by the broad diffraction peak at 9.5 to 11 degrees 2θ for glycolated samples. For the Edmonton samples, this peak is quite pronounced, in some instances being almost as intense as the illite peak. In the Olds samples, the presence of interstratified clay minerals is less pronounced and restricted to sites 1 and 2. Sites 3 and 4 in the Olds area, which were found to be high in chlorite do not show evidence of interstratification. X-ray diffraction patterns of clay samples from the Pincher Creek C horizons suggest the presence of interstratification as evidenced by the broad diffraction peak at 9.5 to 11 degrees 2θ , however these peaks are very weak. Compared to the Edmonton samples, Olds and Pincher Creek samples contain lower amounts of interstratified clay minerals in the C horizons.

That interstratified clay minerals exist in Western Canadian parent materials is verified by the work of Lavkulich (1963), St. Arnaud

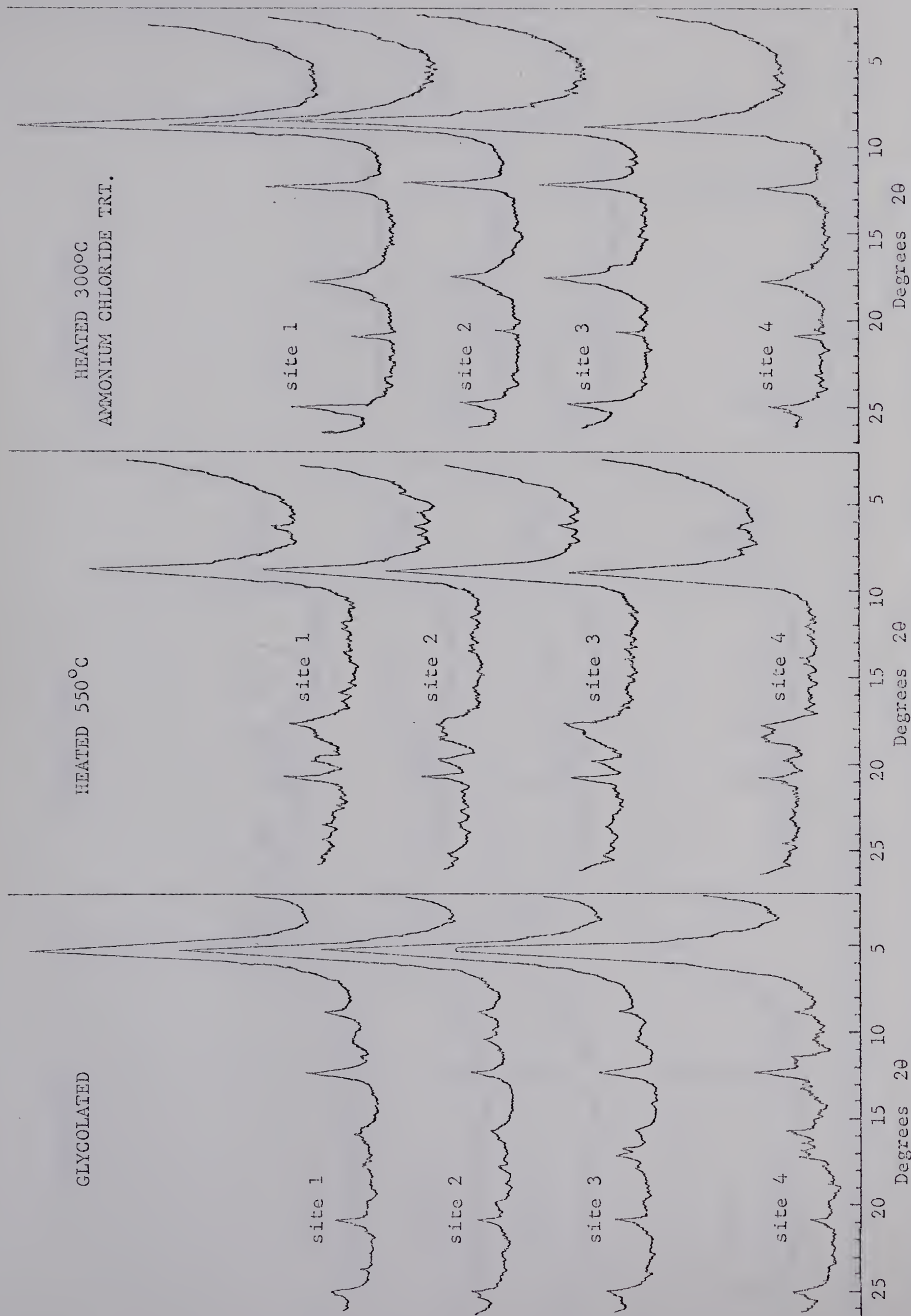


Figure 11 X-ray diffraction patterns of total clay separated from the C_{ca} horizon - Edmonton area.

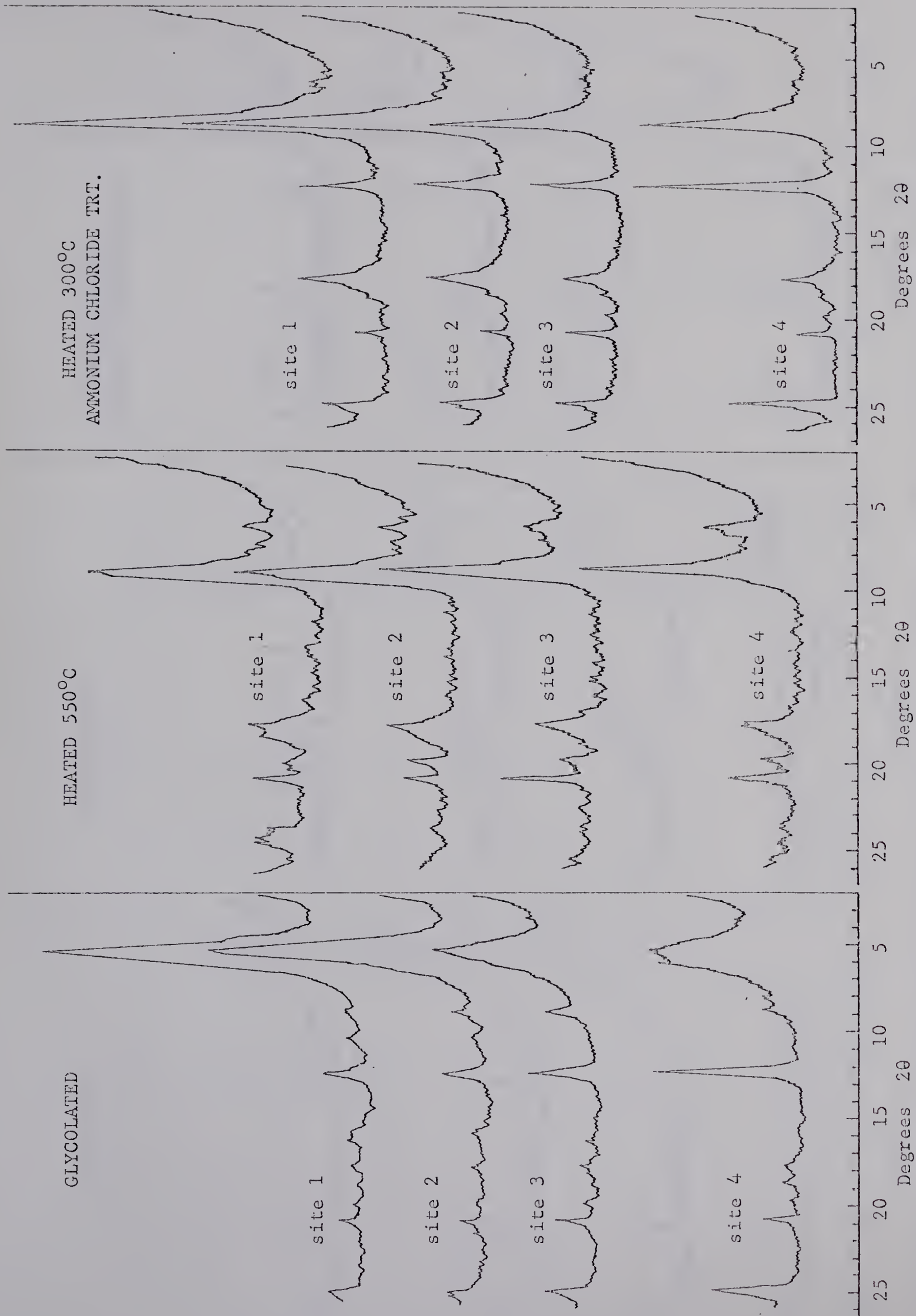


Figure 12 X-ray diffraction patterns of total clay separated from the C_{ca} horizon - Olds area.

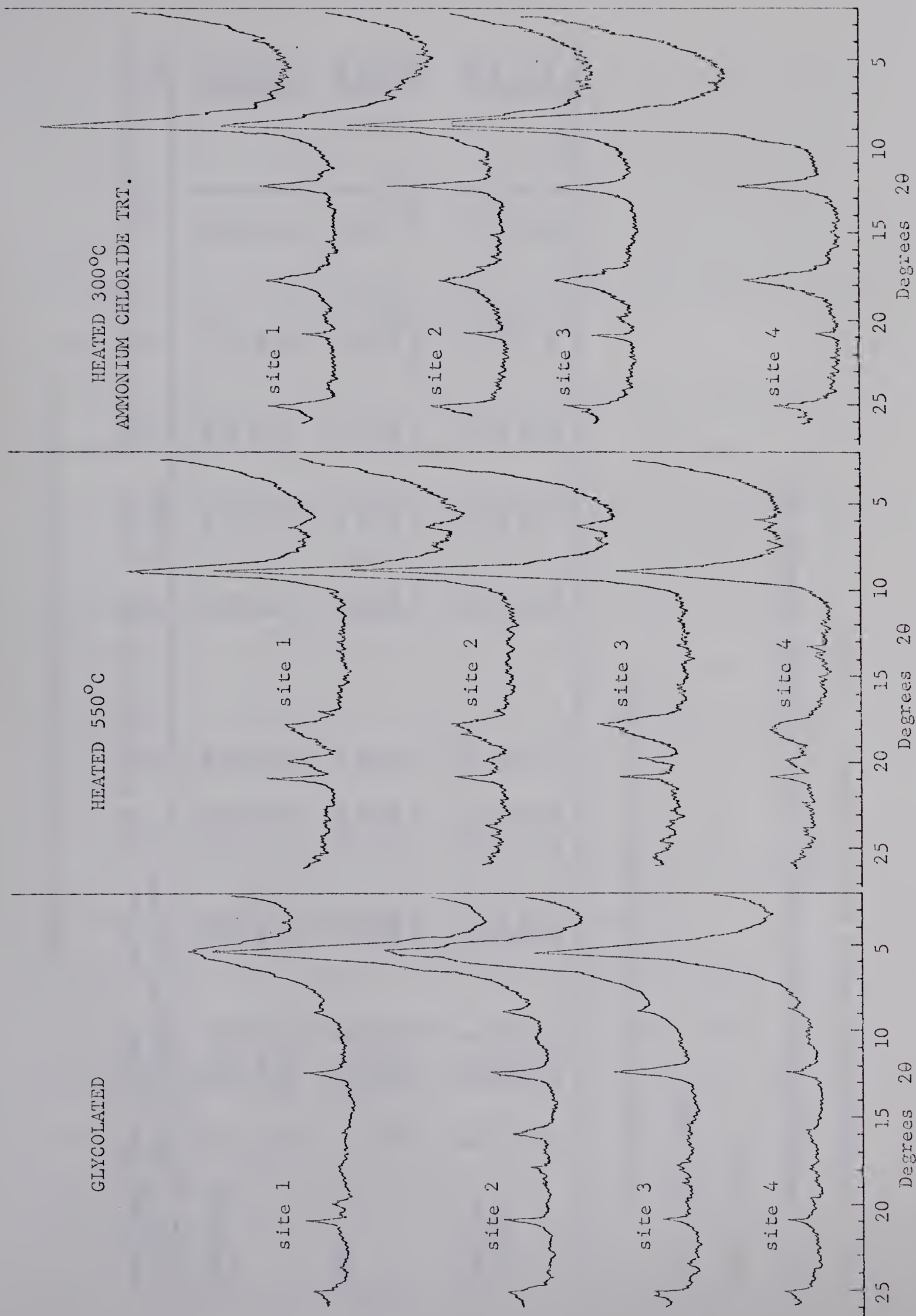


Figure 13 X-ray diffraction patterns of total clay separated from the C_{ca} horizon - Pincher Creek area.

TABLE VII. Clay Mineral Analyses of C Horizons

Sampling area	Site no.	Total C.E.C. **	Surface area***	K ₂ O %	% Montmorillonite (1)	% Montmorillonite (2)	% Mont. (mean)	Illite %	Chlorite* %	Kaolinite* %	Quartz* %
Edmonton	1	58.4	697	2.36	60	70	65	24	5-10	0-4	2-6
	2	68.2	760	1.98	72	76	74	20	2-5	0-2	2-6
	3	63.7	659	2.21	67	66	67	22	4-7	0-4	2-6
	4	66.0	763	1.70	70	76	73	17	3-7	0-4	2-6
Olds	1	69.8	774	1.88	74	77	76	19	2-6	0-2	2-6
	2	67.0	716	1.27	72	72	72	13	4-8	0-2	2-6
	3	52.6	560	2.32	54	56	55	23	5-15	0-5	2-6
	4	51.7	514	1.95	54	51	52	20	10-20	0-10	2-6
Pincher Creek	1	66.3	618	2.56	69	62	66	26	2-6	0-2	2-6
	2	59.3	634	2.19	62	63	62	22	5-10	0-5	2-6
	3	61.8	621	1.81	65	62	64	18	5-10	0-5	2-6
	4	67.4	725	2.14	71	72	72	21	0-5	0-2	2-6

* Estimates based on X-ray diffraction patterns

** me./100 g

*** m²/g

(1) Montmorillonite values based on cation exchange capacity data

(2) Montmorillonite values based on surface area data

et al. (1963), and Kodama et al. (1965). Kodama et al. (1965) conducted an intensive study of interstratified clay minerals from subsoils in the Canadian Prairie Provinces. Their results suggest the presence of randomly interstratified layers of montmorillonite and mica and that the expandable layers are probably intermediate between montmorillonite and beidellite in composition.

Differential thermographs of the total clay fraction separated from the C horizons are shown in Figures 14 to 16. The basic similarity of these thermographs also suggests that the clay mineralogy of the C horizons is quite uniform in the three sampling areas. Some variation in the initial two endothermic peaks is evident. But this variation simply reflects differences in hydration of the clay. When thermographs for samples were prepared by D. T. A. immediately after freeze-drying of the clay, the two endotherms representing dehydration were noticeably decreased in intensity.

The thermographs all have hydroxyl endotherms between 500° and 590° C typical of illitic minerals. However "abnormal" montmorillonites (Bose, 1954; Cole, 1955; St. Arnaud, 1963; Kodama et al., 1965) could also show peaks in the same range. Beidellite gives its main hydroxyl endothermic peak in the 550° C region (St. Arnaud, 1963). Arshad (1964) described montmorillonite in some Alberta soils as beidellitic in nature. Interstratified montmorillonite-illite also gives a 540° C endothermic peak (Cole, 1955). Very similar thermographs, to those reported in this study,

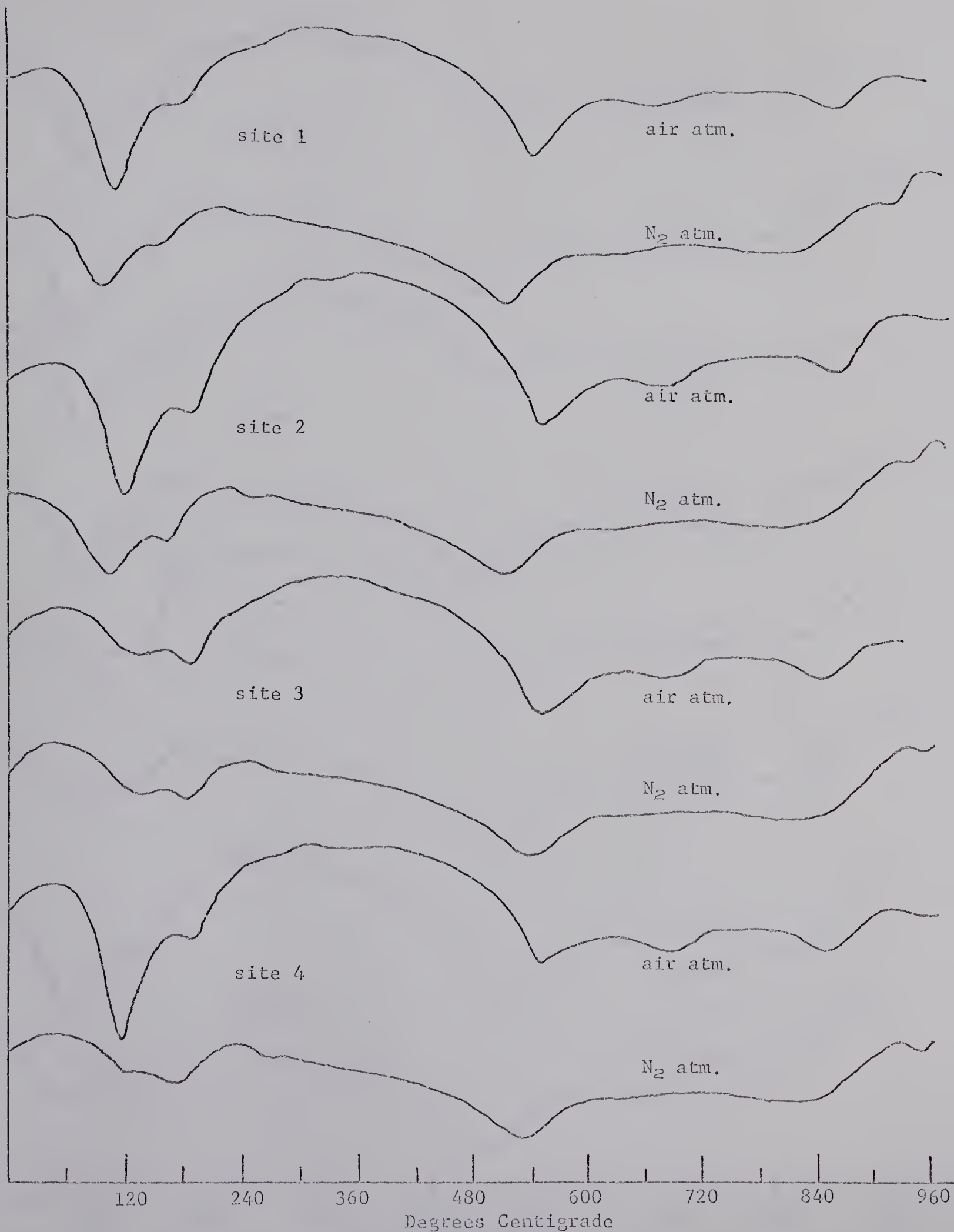


Figure 14 Differential thermographs of the total clay fractions separated from the C_{ca} horizon - Edmonton area.

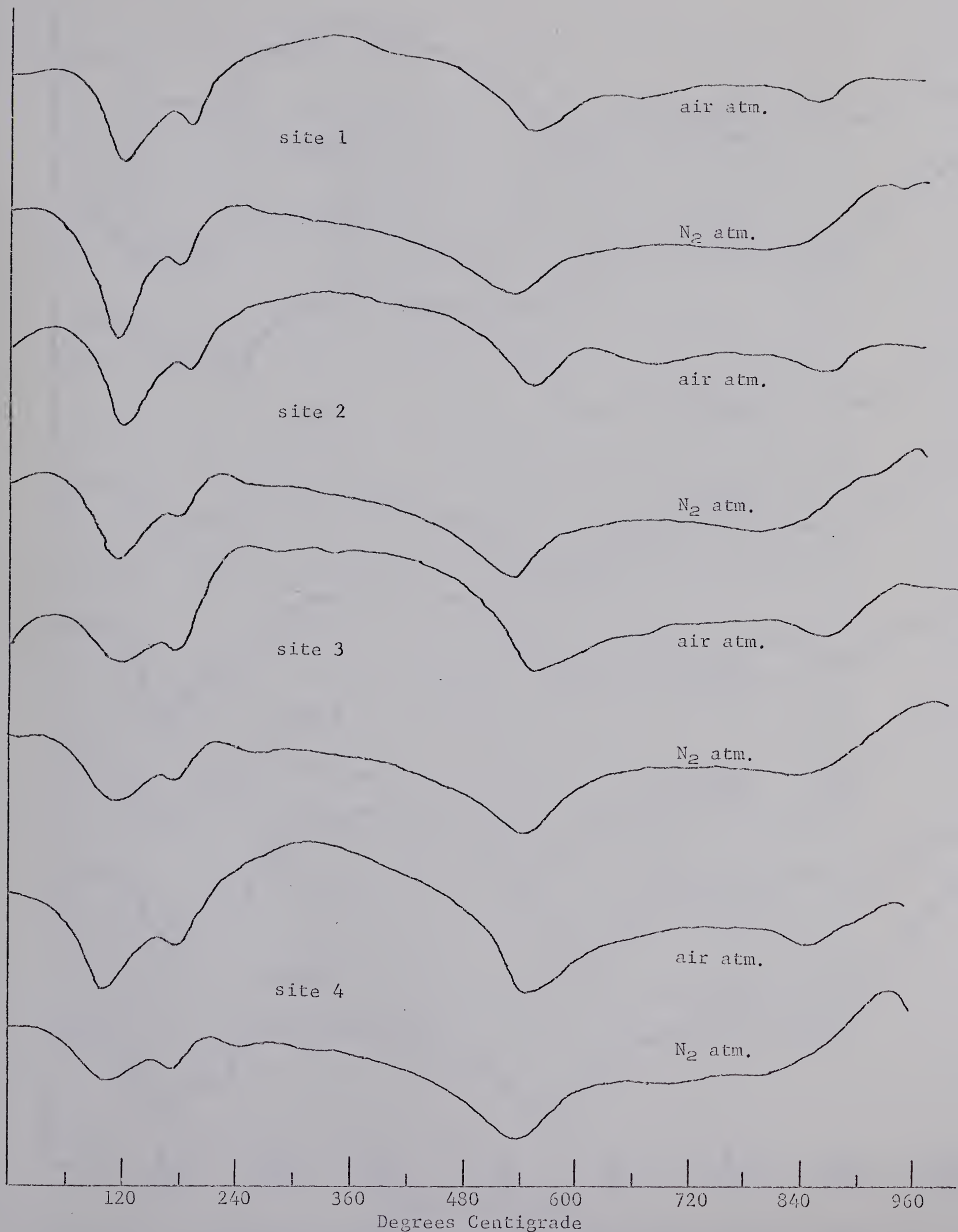


Figure 15 Differential thermographs of the total clay fractions separated from the C_{ca} horizon - Olds area.

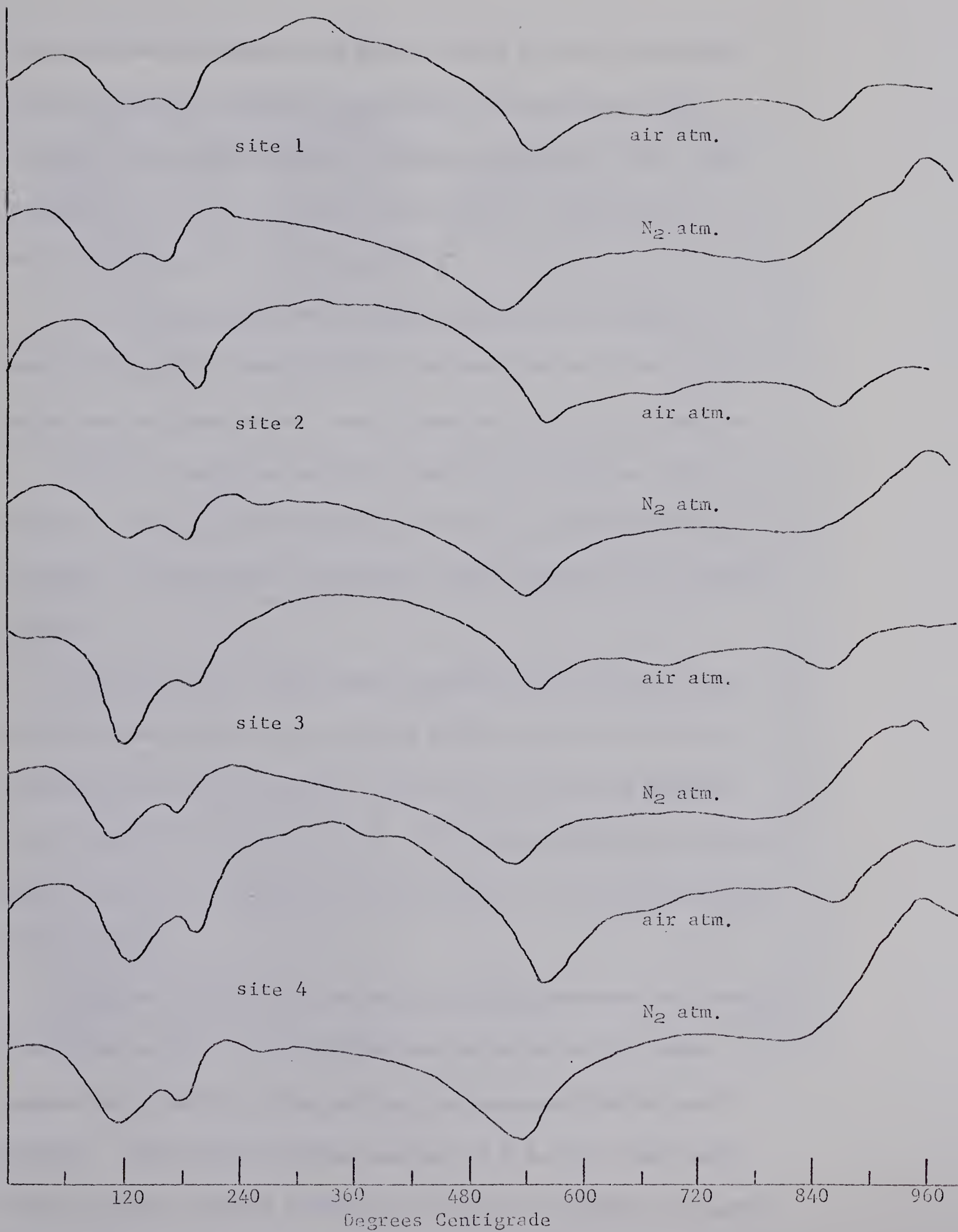


Figure 16 Differential thermographs of the total clay fraction separated from the C_{ca} horizon - Pincher Creek area.

were obtained by Kodama and Brydon (1963) for clays separated from till samples obtained from Alberta, Saskatchewan and Manitoba. The authors report endothermic peaks at 120°, 190° (shoulder), 535°, 650° (inflexion) and 880° C. Exothermic peaks were reported at 310° and 910° C.

The thermographs thus indicate the presence of illite or montmorillonite or interstratified montmorillonite-illite, or all three, and substantiate the results obtained from X-ray analysis.

Plate 9 consists of selected electron micrographs which illustrate various clay minerals found in the parent material (C horizons). The presence of kaolinite was verified by micrograph 3 and 4.

X-ray analysis, differential thermal analysis and surface area determinations were conducted on the total clay fractions separated from the B horizons. The X-ray diffraction patterns are presented in Figures 17 to 19. The differential thermographs are presented in Figures 20 to 22 and surface areas are presented in Table VIII.

In general, the clay mineralogy of all B horizons was found to be quite similar. X-ray diffraction patterns for the clays suggest the presence of high amounts of montmorillonite in all samples. Differential thermal analysis of B horizon clays gave results similar to those obtained for C horizon samples. Specific differences in the differential thermal curves were noted by the

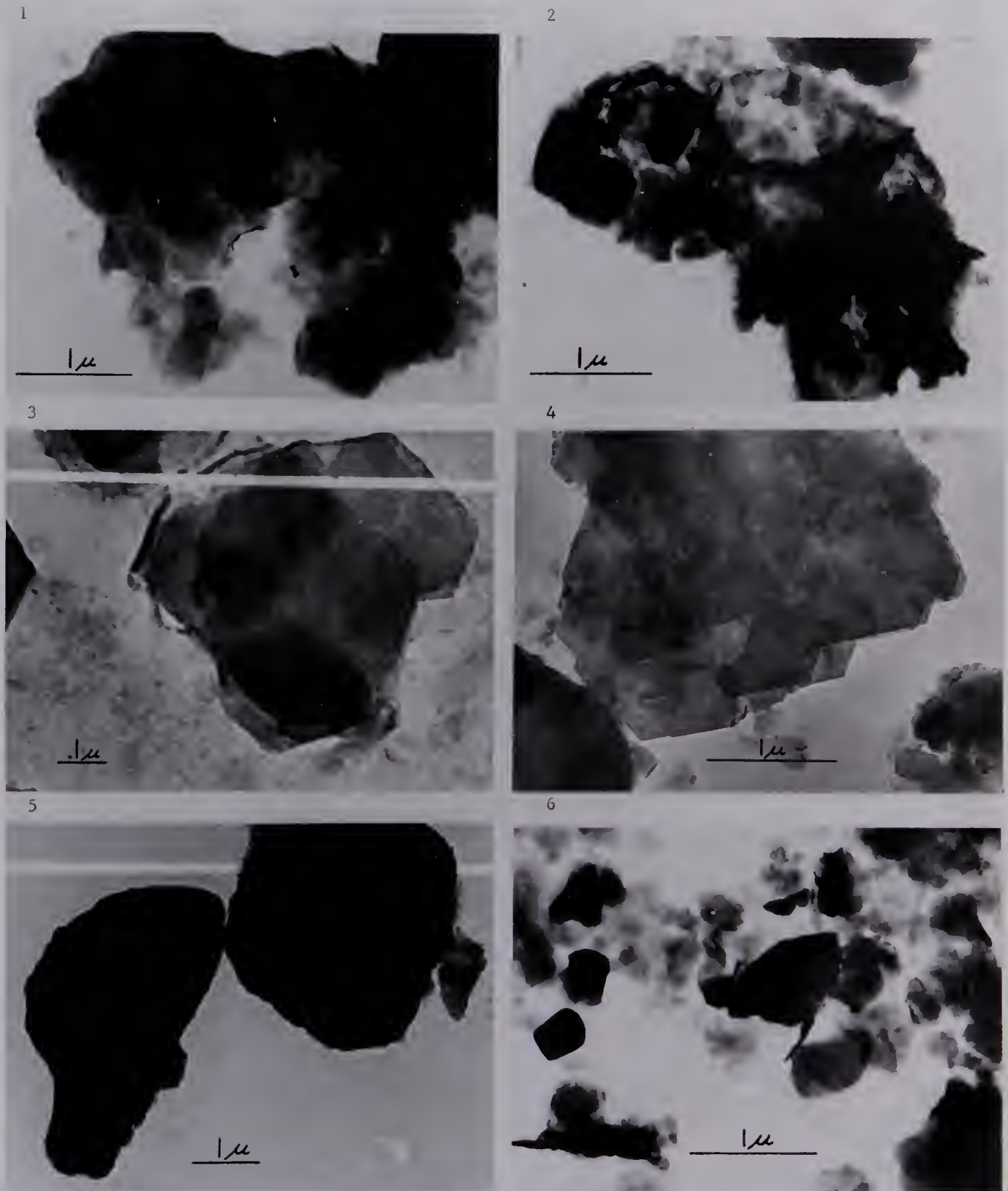


Plate 9 Electron micrographs of clay minerals found in the parent material of the three sampling areas.

Description of Plate 9

- Photograph 1. Electron micrograph showing the most commonly encountered clay mineral in the parent material of the three sampling areas. According to the A.P.I. Standards (1951), this is a micrograph showing features typical of montmorillonite.
- Photograph 2. Electron micrograph showing features typical of montmorillonite clay minerals. This mineral was observed in all clay fractions studied.
- Photograph 3. Electron micrograph of kaolinite found in the parent material of the three sampling areas.
- Photograph 4. The presence of kaolinite in the parent material is depicted by this electron micrograph. The well-defined hexagonal cleavage angles indicate the mineral is kaolinite. A small kaolinite particle is observable in the lower right hand corner.
- Photograph 5. Electron micrograph showing the presence of illite and/or chlorite in the parent material. Although montmorillonite may take on a rounded aspect, the well-defined edges of the minerals in this micrograph indicate illite and/or chlorite.

Photograph 6. Electron micrograph generally showing a variety of montmorillonite particles. Some of the particles with well-defined edges are illite.

HEATED

GLYCCLATED

site 1

site 1

site 2

site 2

site 3

site 3

site 4

site 4

Degrees 2θ

Degrees 2θ

Figure 17 X-ray diffraction patterns of total clay separated from the Bm horizon - Edmonton area.

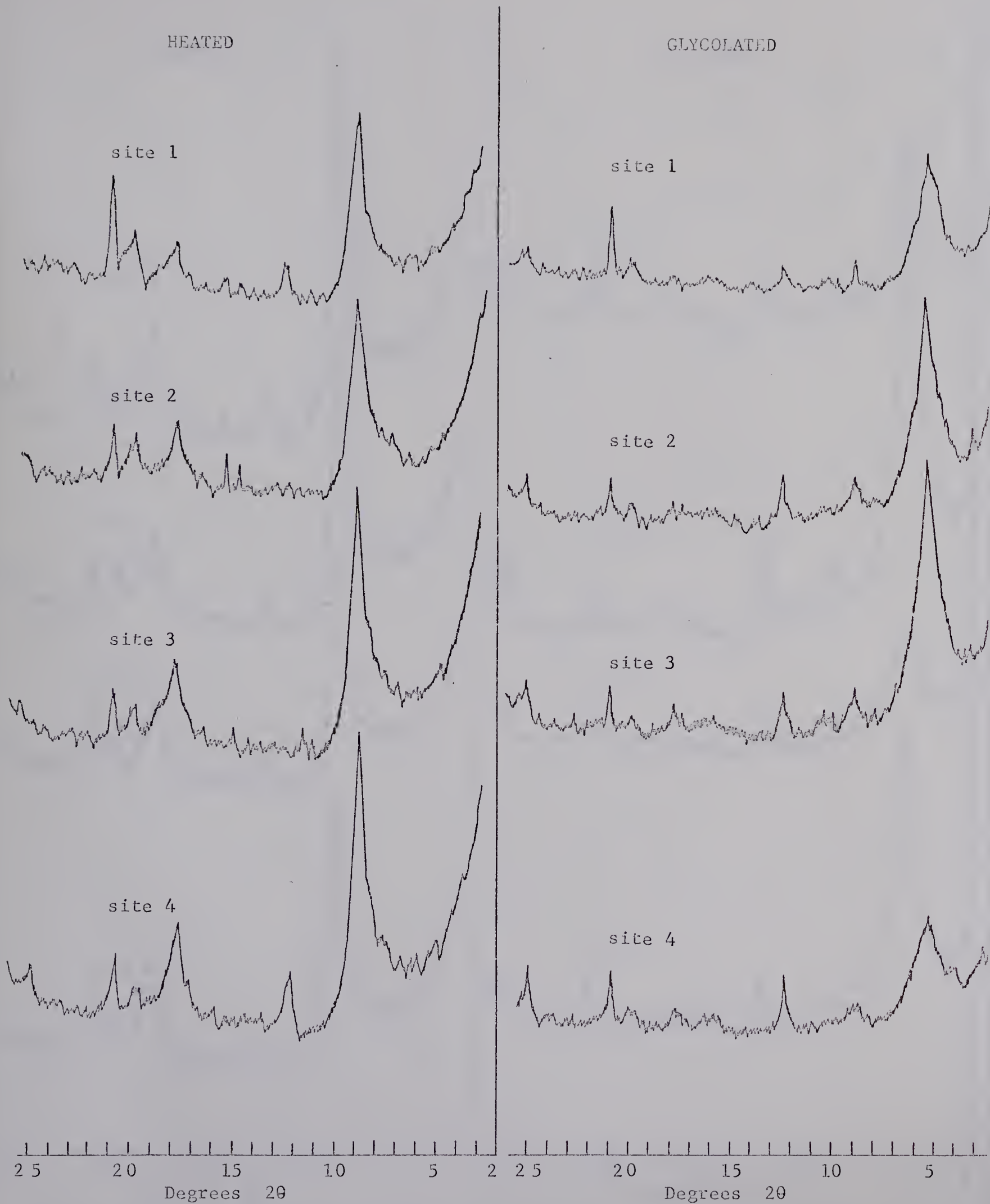


Figure 18 X-ray diffraction patterns of total clay separated from the Bm horizon - Olds area.

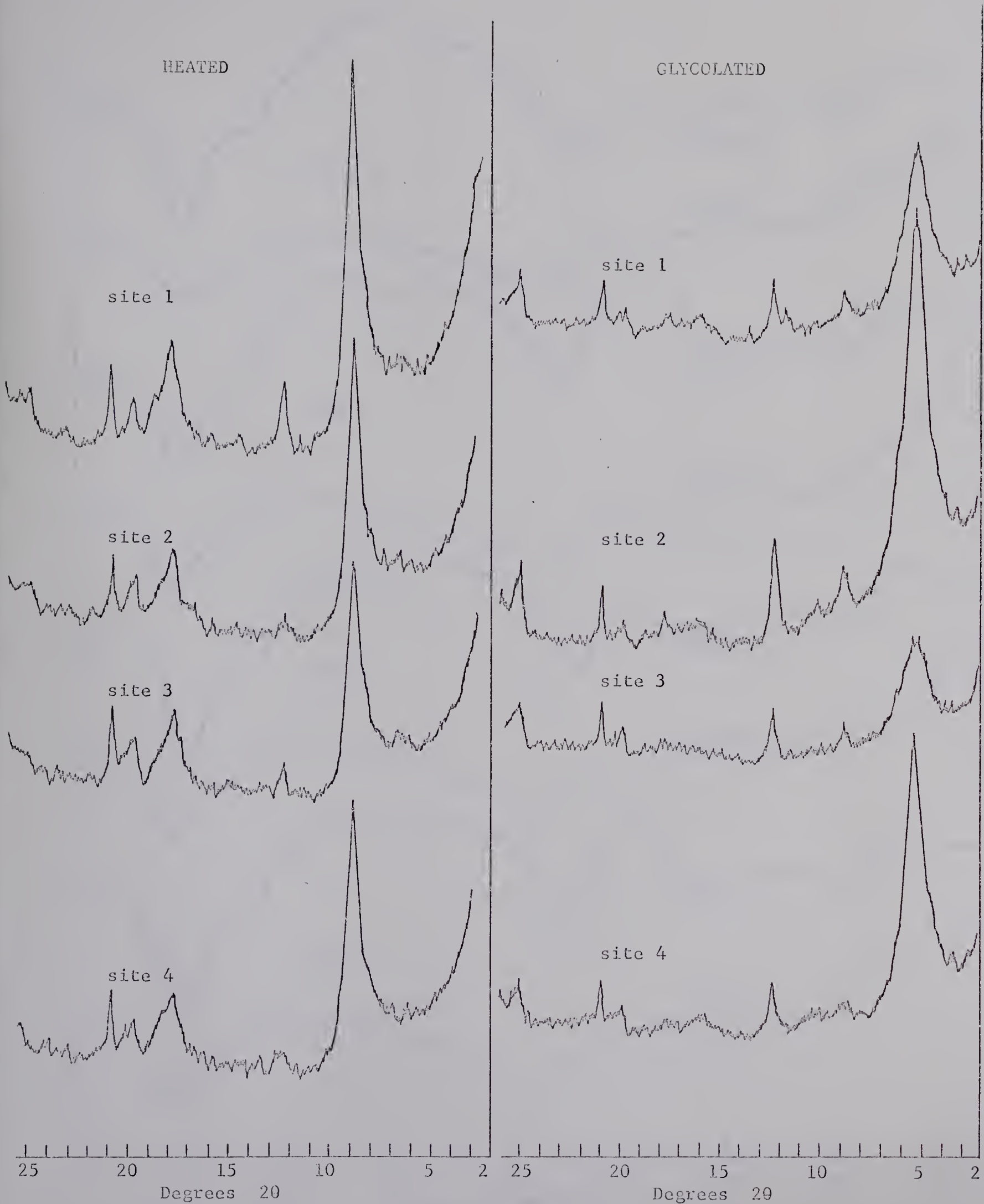


Figure 19 X-ray diffraction patterns of total clay separated from the Bm horizon - Pincher Creek area.

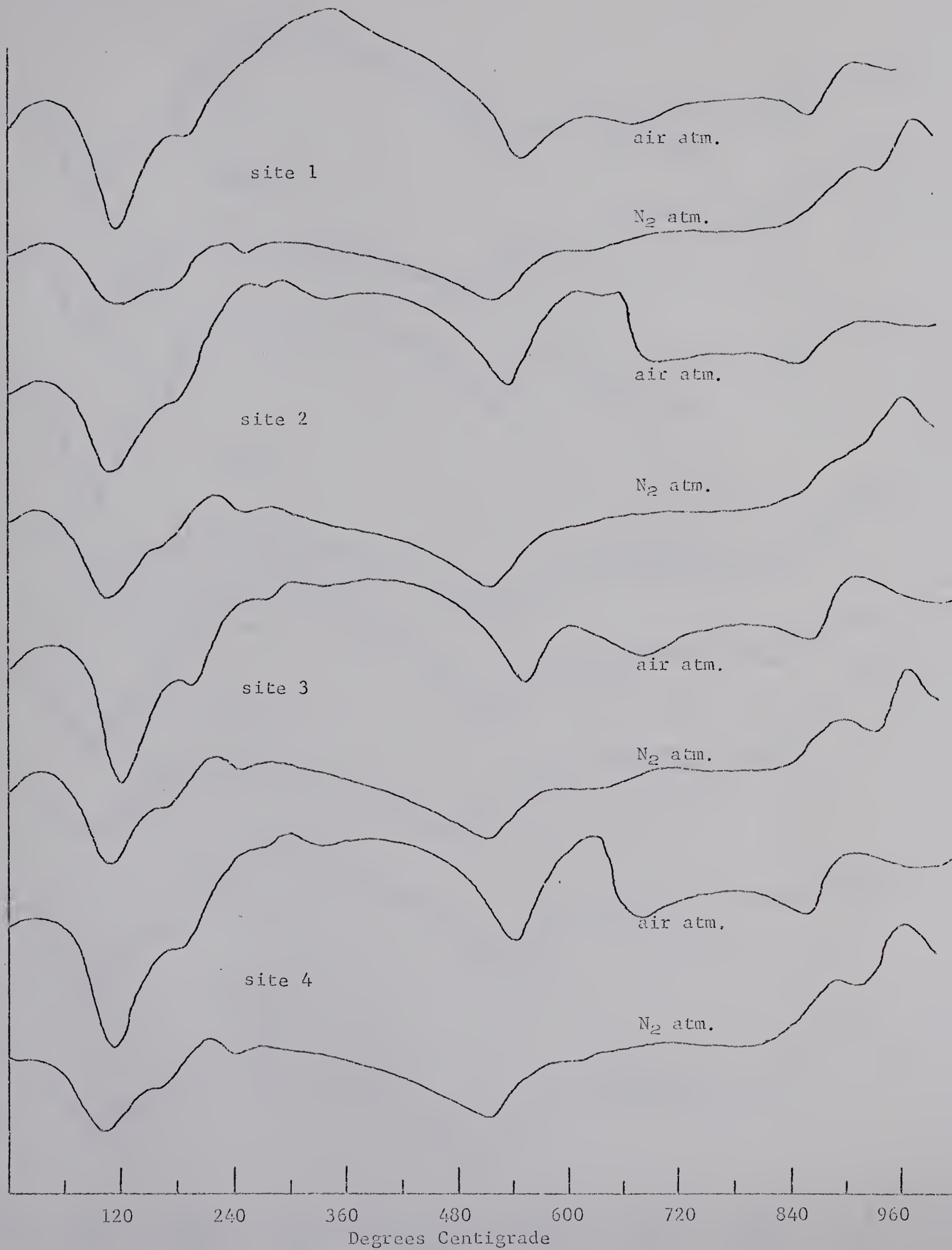


Figure 20 Differential thermographs of the total clay fraction separated from the Bm horizon - Edmonton area.

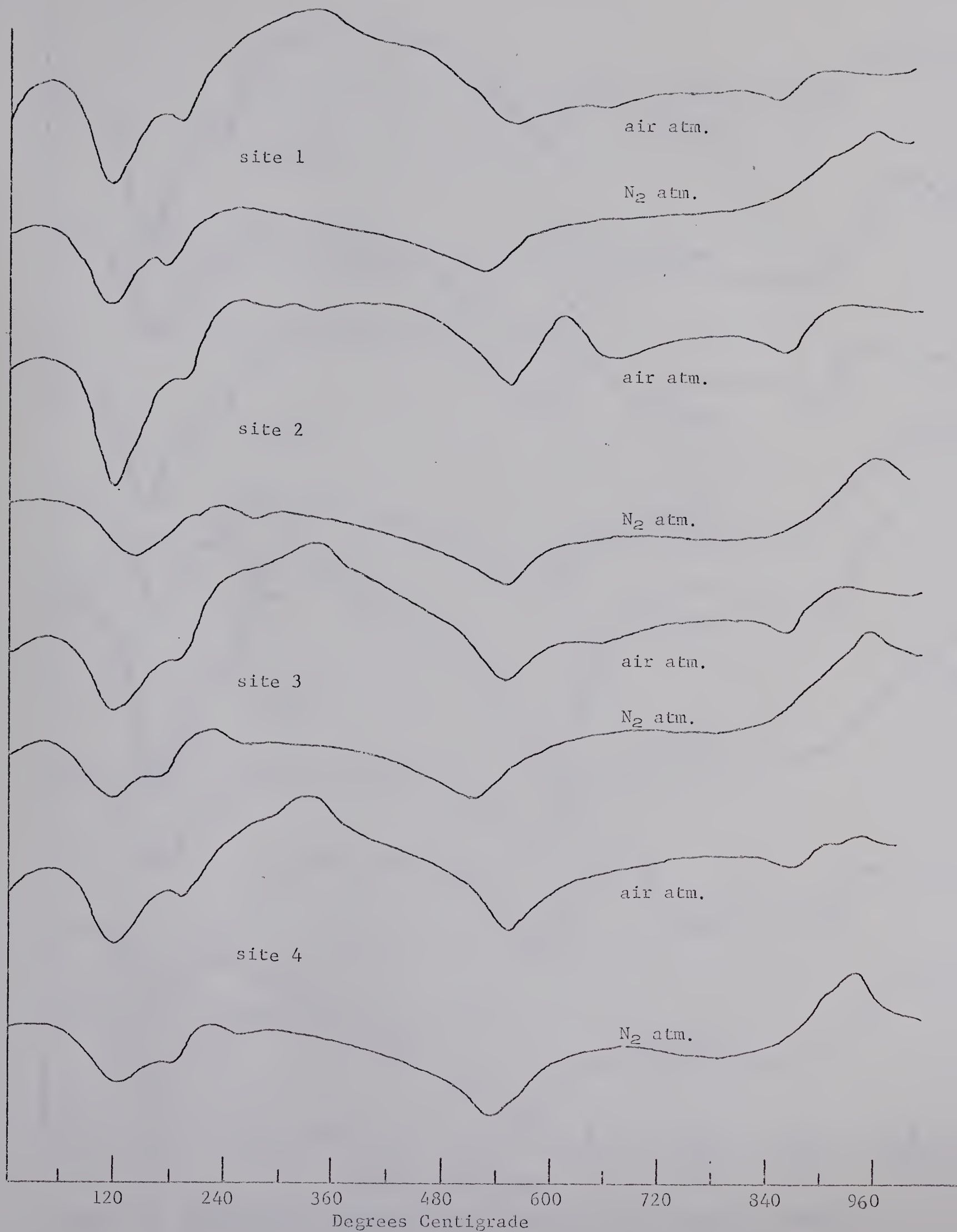


Figure 21 Differential thermographs of the total clay fraction separated from the Bm horizon - Olds area.

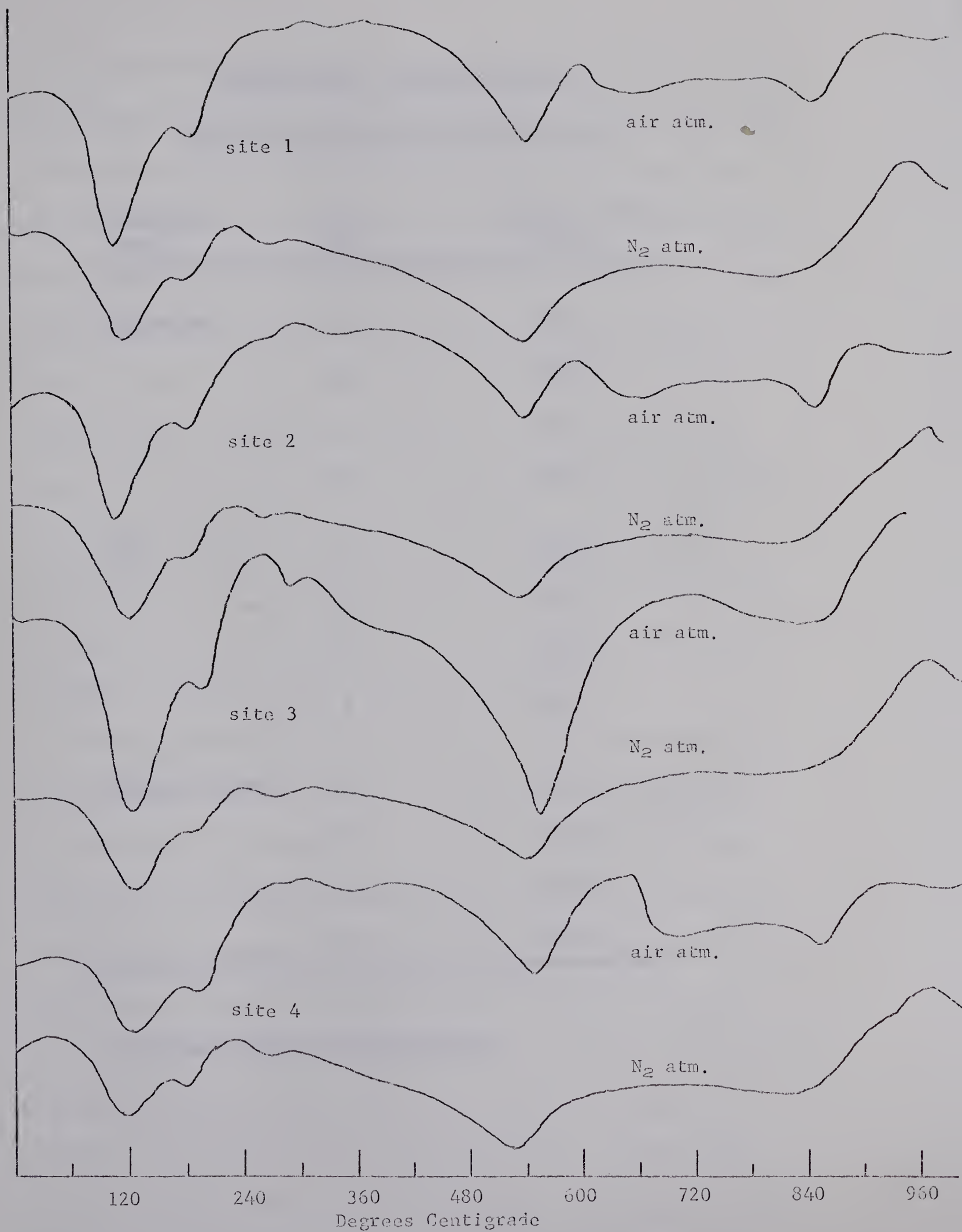


Figure 22 Differential thermographs of the total clay fraction separated from the Bm horizon - Pincher Creek area.

TABLE VIII. Surface Areas of
Total Clay Separated from B Horizons

Sampling area	Site no.	Surface Area* m ² /g
Edmonton	1	651
	2	605
	3	643
	4	570
Olds	1	507
	2	599
	3	615
	4	603
Pincher Creek	1	527
	2	548
	3	508
	4	593

* average of three determinations

appearance of broad exothermic peaks in the 220° to 360° C range for B horizon samples. This exothermic peak was weak or lacking in C horizon samples. When B horizon clays were analyzed on the D.T.A. using an oxygen atmosphere (O₂ flow rate of 40 cc per min.) these peaks were enhanced considerably. Exothermic peaks in this region are likely the result of the combustion of organic matter (Mathieu, 1960). Samples from the C horizons exhibited weak 650-700° C endothermic inflexions. In B horizon samples many of the thermographs show a sharp drop at the 660° C portion of the curve resulting in a broad endothermic peak in the 680°-860° C region. The explanation for this endothermic reaction for B horizon clays is not available but the effect of iron oxide and/or the effect of organic matter should be considered.

Some specific differences were noted between the total clay fraction from B and C horizons. In the glycolated samples from the B horizons, some broad 17 Å diffraction peaks are evident. Brown (1961) has suggested that organic molecules can enter into the interlattice spacings of montmorillonite. The suggestion has been made by Lavkulich (1963) and Arshad (1964) that naturally occurring organic molecules in the interlattice spacings may prevent complete glycolation to give sharp 17 Å peaks. Although it is possible that weathered illite could be responsible for the broad 17 Å peak (White, 1950), it is felt that organic interlayering is a more likely explanation. This is partially substantiated by the

differential thermographs (Figs. 21-23) where the broad exothermic peaks in the 200° to 380° C range were attributed to organic matter combustion. Glycolated clay samples from the C horizon showed well-defined, sharp 17 Å peaks. Although K₂O content was not determined on B horizon clays, it is evident from the X-ray diffraction patterns that the relative illite content is slightly lower than the content in the C horizon clays. Although X-ray data suggest a slight relative decrease in illite content of B horizon clays, this is not substantiated by the surface area values which were found to be slightly lower than surface area values for C horizon clays. If organic matter was complexed to clays from the B horizons as was suggested, surface areas would be reduced (Burford, 1964) thereby invalidating semiquantitative estimation of montmorillonite on the basis of surface area.

Mechanical analysis (Tables IIa to IVa) suggest a slight clay accumulation in the B horizons. Morphologically, many of the B horizons were described as weakly textural (Btj) horizons. From X-ray data, mechanical analysis, and morphological descriptions, it appears that accumulation of clays has occurred in B horizons.

Small but significant peaks evident in the 2 to 4 degrees 2 θ region along with broad peaks in the 9.5 to 11 degrees 2 θ region of the diffractograms indicate the presence of interstratified clay minerals. Similar interstratification was noted for C horizon clays.

Chemical and Mineralogical Characteristics of the Clay Fractions
Separated from Ah₂ Horizons

Total clay samples from the pooled Ah₂ horizons were separated into 2 - 1 micron, 1 - 0.2 micron and 0.2 - 0.08 micron fractions in order to determine the nature and degree of clay-organic matter complex formations. The clay fractions were then subjected to X-ray, differential thermal, cation exchange, free iron and aluminum, fusion, surface area, infrared and electron microscopic analysis.

X-ray analysis of clay fractions. X-ray diffraction patterns of untreated clay fractions are presented in Figures 23 and 24. Diffraction patterns for heated and glycolated samples show that the clay fractions are composed predominantly of montmorillonite and illite with low amounts of kaolinite and chlorite. The presence of chlorite and interstratified clays are suggested by the occurrence of weak peaks and shoulders in the 3 to 8 degrees 2θ region for heated samples. These peaks and shoulders are most pronounced in the coarse clay fraction and are less obvious with decreasing size fraction. Glycolated samples show broad, shouldered 17 Å diffraction peaks for samples from the Pincher Creek and Olds sites. This indicates organic interlayering, interstratification and/or weathering of illite as previously suggested. Edmonton samples show well-defined, sharp 17 Å diffraction peaks for all fractions. Visser (1965) studied the effect of long term incubation of montmorillonite with decomposing

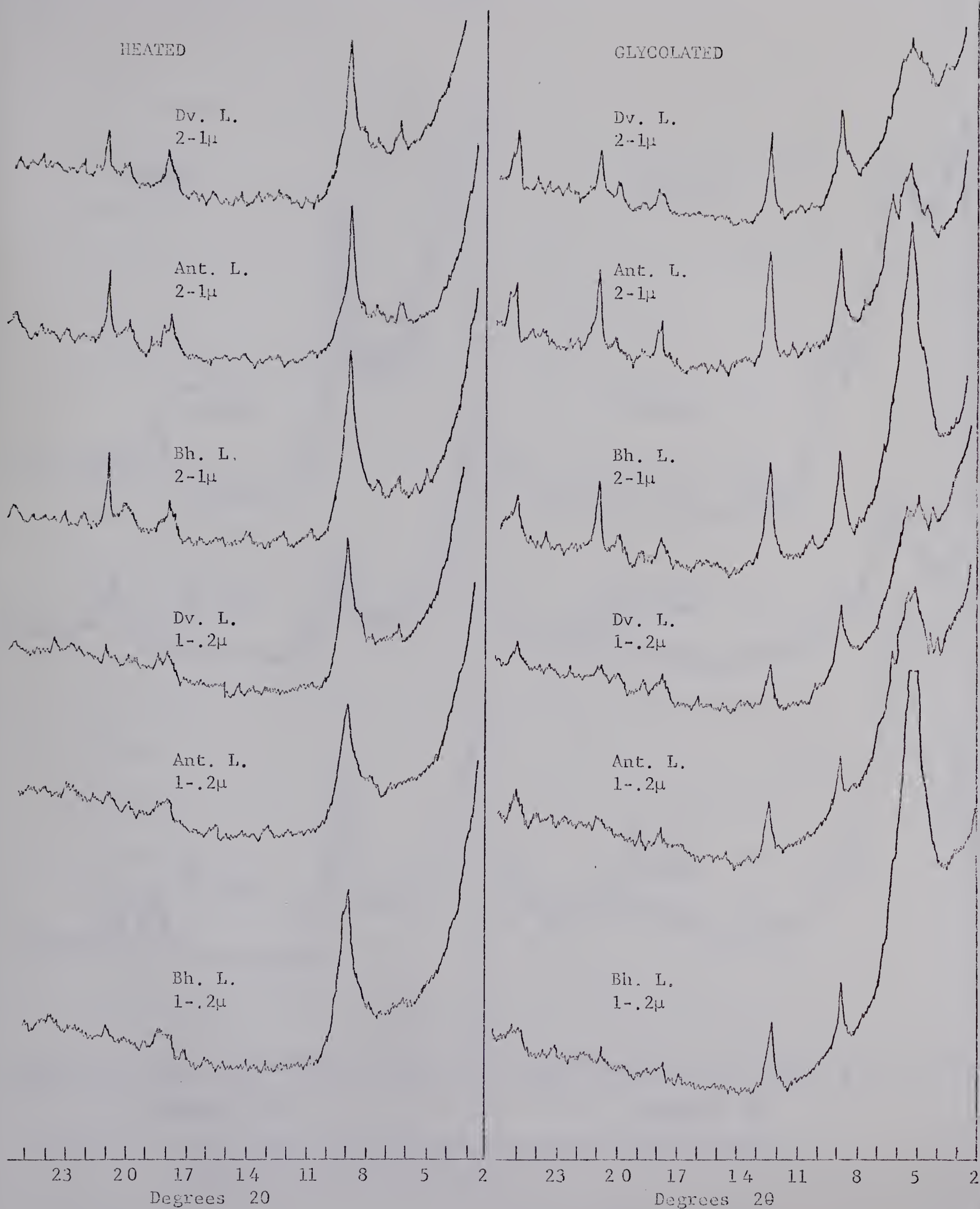


Figure 23 X-ray diffraction patterns of untreated clay fractions separated from the Ah₂ horizon.

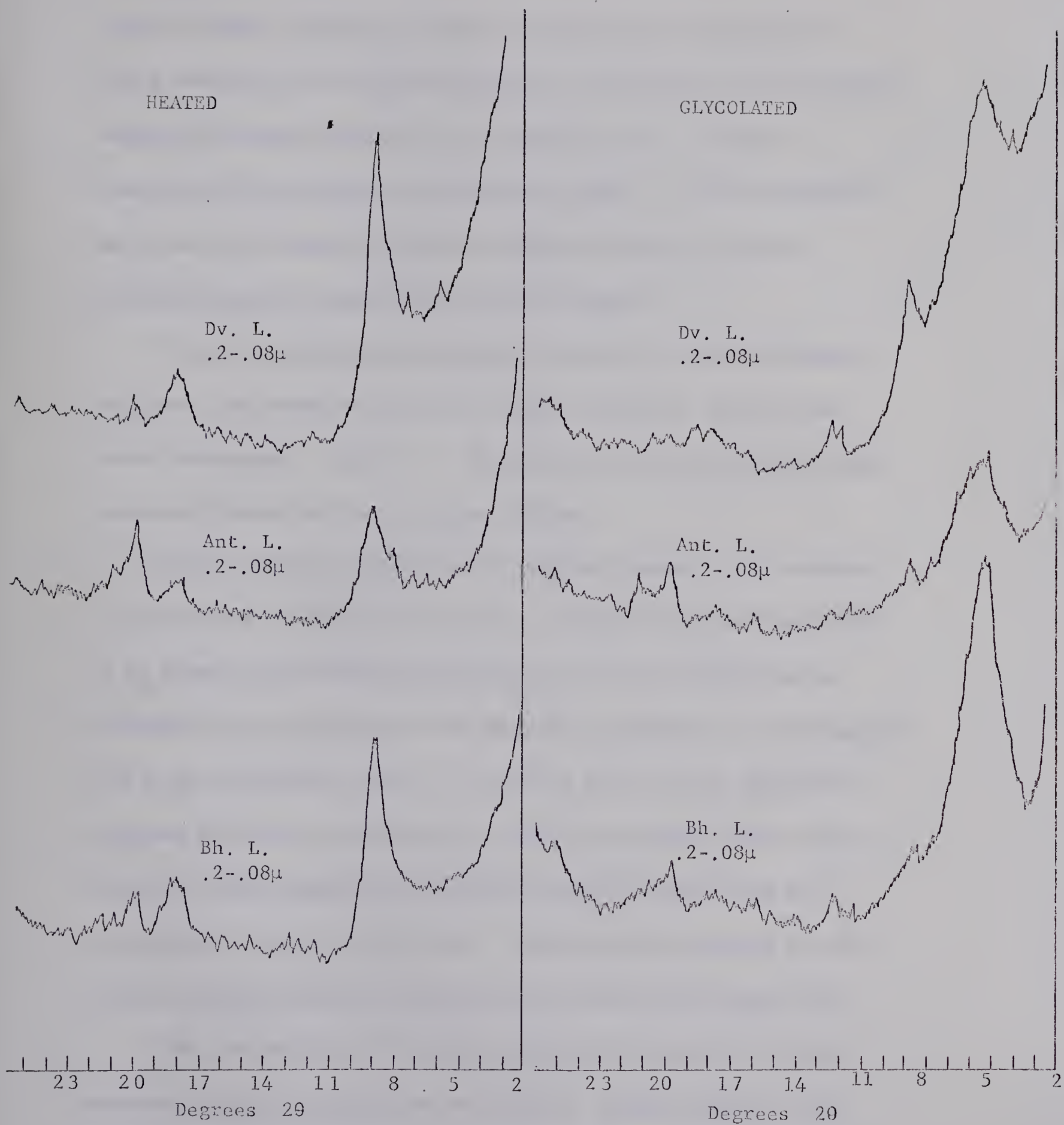


Figure 24 X-ray diffraction patterns of untreated clay fractions separated from the Ah₂ horizon.

organic matter. Montmorillonite that had been incubated for 7 years showed on X-ray diffractograms a broad peak of low intensity, ranging from approximately 4 to 7 degrees 2θ . Peroxide treatment did not enhance the diffraction peak. Visser attributed the broad, low intensity peak for montmorillonite to organic interlayering and weathering of the clay lattice.

The X-ray diffraction patterns showed that with decreasing clay size, the relative amounts of illite, koalinite, chlorite and quartz decreased. The 0.2 - .08 micron fraction is predominantly montmorillonite with low amounts of illite.

X-ray diffraction patterns of peroxide treated clay fractions are presented in Figures 25 and 26. Peroxide treatment had little or no effect on the diffraction patterns of the clay separates as indicated by the similarity of the diffraction patterns. This suggests that if the broadening of the 17 Å peak as observed for glycolated samples was due to interlayered organic compounds, that organic material would occupy interlamellar positions which were not susceptible to attack by peroxide. Carbon determinations for the treated samples further substantiate this conclusion (Figure 33).

The composition of the clay mineral fractions for the three sampling areas are presented in Table X. Illite content of clay fractions separated from the Pincher Creek Ah₂ samples is higher than in samples from the Olds and Edmonton areas. The illite



Figure 25 X-ray diffraction patterns of peroxide treated clay fractions separated from the Ah₂ horizon.

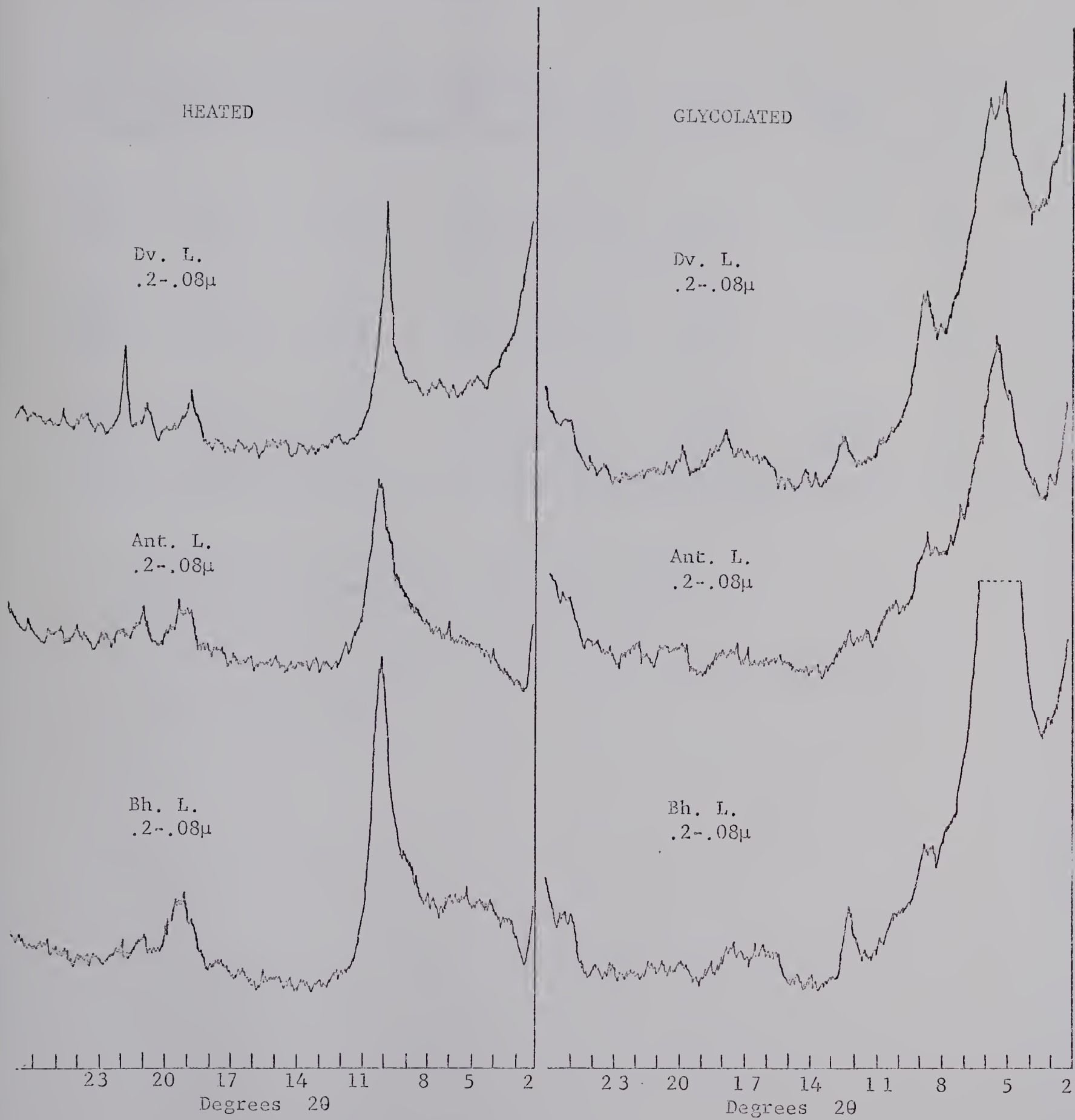


Figure 26 X-ray diffraction patterns of peroxide treated clay fractions separated from the Ah₂ horizon.

TABLE IX. Clay Mineral Analyses of the

Sampling area	Clay fraction	K ₂ O %	Readily extractable Al ₂ O ₃ %	Readily extractable Fe ₂ O ₃ %	C.E.C. me./100 g	Surface area m ² /g
Edmonton	2 - 1 μ	2.44	.93	.67	37.1	248
	1 - .2μ	2.12	1.00	.68	47.5	467
	.2 - .08μ	2.00	1.10	.74	59.0	610
Olds	2 - 1 μ	2.38	.58	1.25	32.1	228
	1 - .2μ	2.29	.62	1.21	44.5	403
	.2 - .08μ	2.16	.62	1.03	53.9	615
Pincher Creek	2 - 1 μ	2.79	1.04	.79	38.0	463
	1 - .2μ	2.94	1.02	.71	43.5	486
	.2 - .08μ	2.90	2.44	.06	56.0	666

Pooled Ah₂ Horizons after H₂O₂ Treatment

Montmorillonite %	Mont. & %	Mont. & (mean)	Illite %	Chlorite*	Kaolinite*	Quartz*	Mont. + Illite
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
25	39	32	24	4- 8	2- 6	4-10	56
46	49	48	21	2- 5	2- 8	2- 6	69
61	62	62	20	2- 4	0- 1	2- 4	82
23	31	27	24	5-15	5-10	4-10	51
40	45	42	23	4- 8	4- 8	2- 6	65
61	56	58	22	0- 4	0- 1	2- 4	80
46	36	41	28	3- 7	5-10	4-10	69
48	42	45	29	5-10	4-12	2- 6	74
66	57	62	29	2- 5	0- 4	2- 4	91

* Estimation based on X-ray diffraction patterns

(1) Montmorillonite values based on surface area data

(2) Montmorillonite values based on cation exchange capacity data

+ For untreated clay

content of Pincher Creek clay fractions separated from Ah₂ horizons is higher compared to the C horizon. This suggests some negative enrichment of illite. The higher chlorite content in the 2 - 1 micron fraction separated from Olds Ah₂ horizons agrees with the higher chlorite content found in the C horizons of the same sites. As the clay size fraction decreases, the content of montmorillonite, as determined by surface area and cation exchange capacity, increases in all three sampling areas. This is in good agreement with X-ray data.

Differential thermal analysis of the untreated clays. Differential thermographs of untreated clay fractions separated from the pooled Ah₂ horizons are shown in Figures 28 and 29.

The initial endothermic peaks, caused by the loss of adsorbed water are essentially the same for all samples. Following the initial endothermic peak is a main exothermic peak at 335° C. This exothermic reaction representing combustion of organic carbon varies in intensity among clay size fractions. The trend indicated by the thermographs is a decrease in the 335° C exothermic peak as the clay size fraction decreases. This was found to be true for all clay fractions from each of the three sampling areas. Following the main 335° C exotherm are a series of peaks and/or inflexion points representing secondary exothermic reactions. These inflexions and peaks are most pronounced in the coarse clay fraction and almost

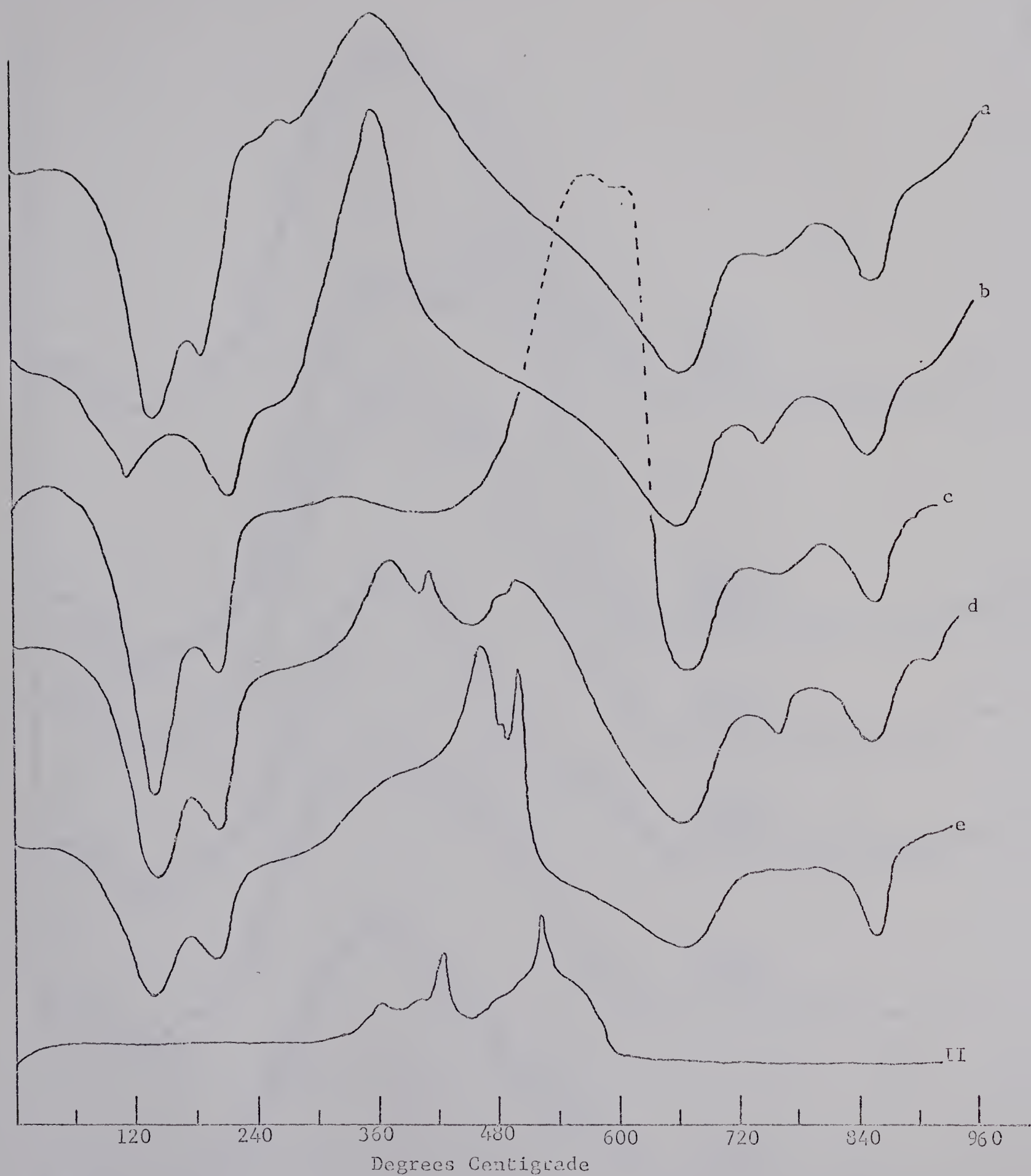


Figure 27 Differential thermographs of Ca-montmorillonite treated with:
(a). 3.5% lactose, aqueous suspension
(b). EGME
(c). 3% carbon, physical mixture
(d). 3% Krilium, physical mixture
(e). 15% Krilium, aqueous suspension
II. 5% Krilium, 95% Al_2O_3 , physical mixture

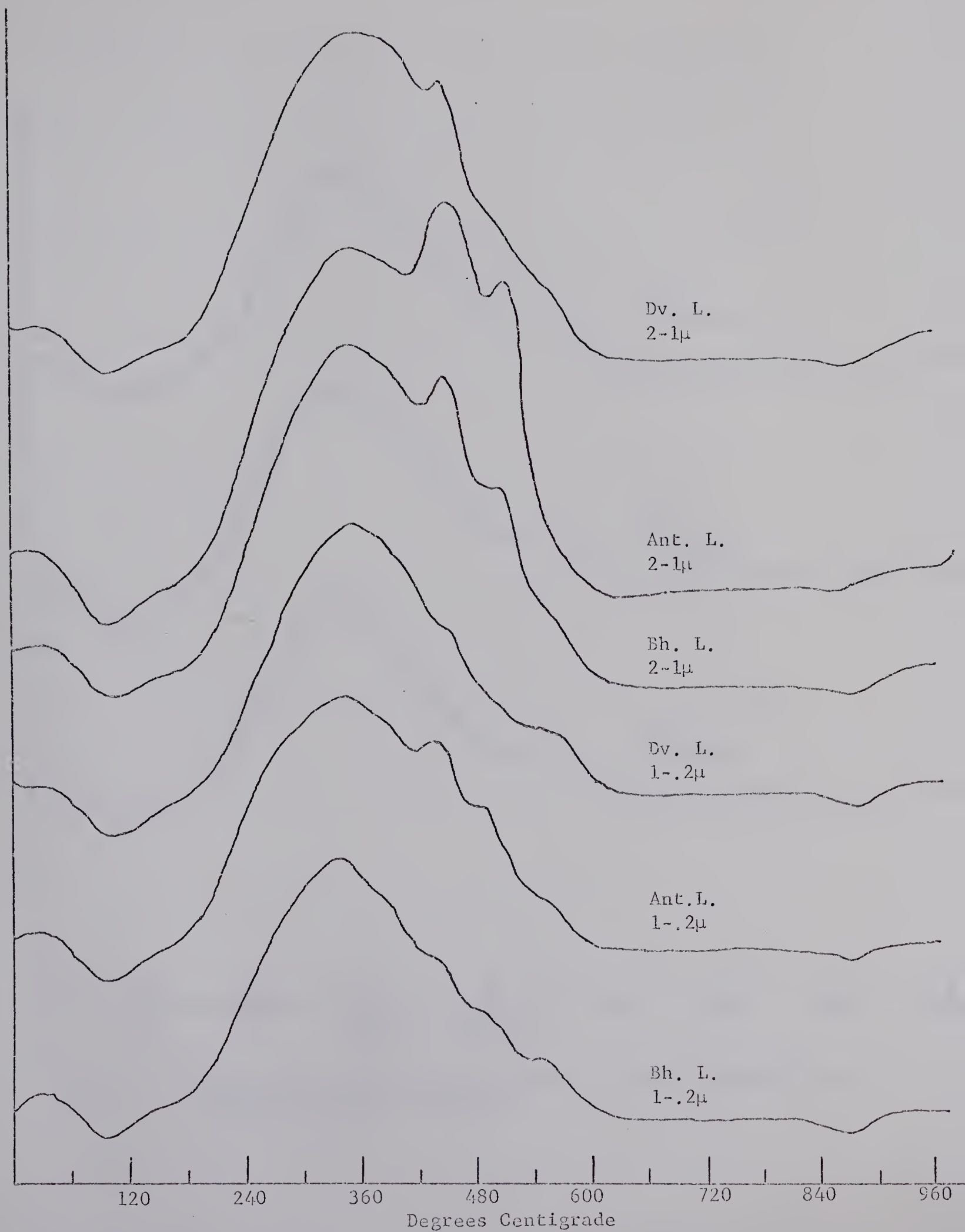


Figure 28 Differential thermographs of clay fractions separated from the Ah₂ horizon - untreated.

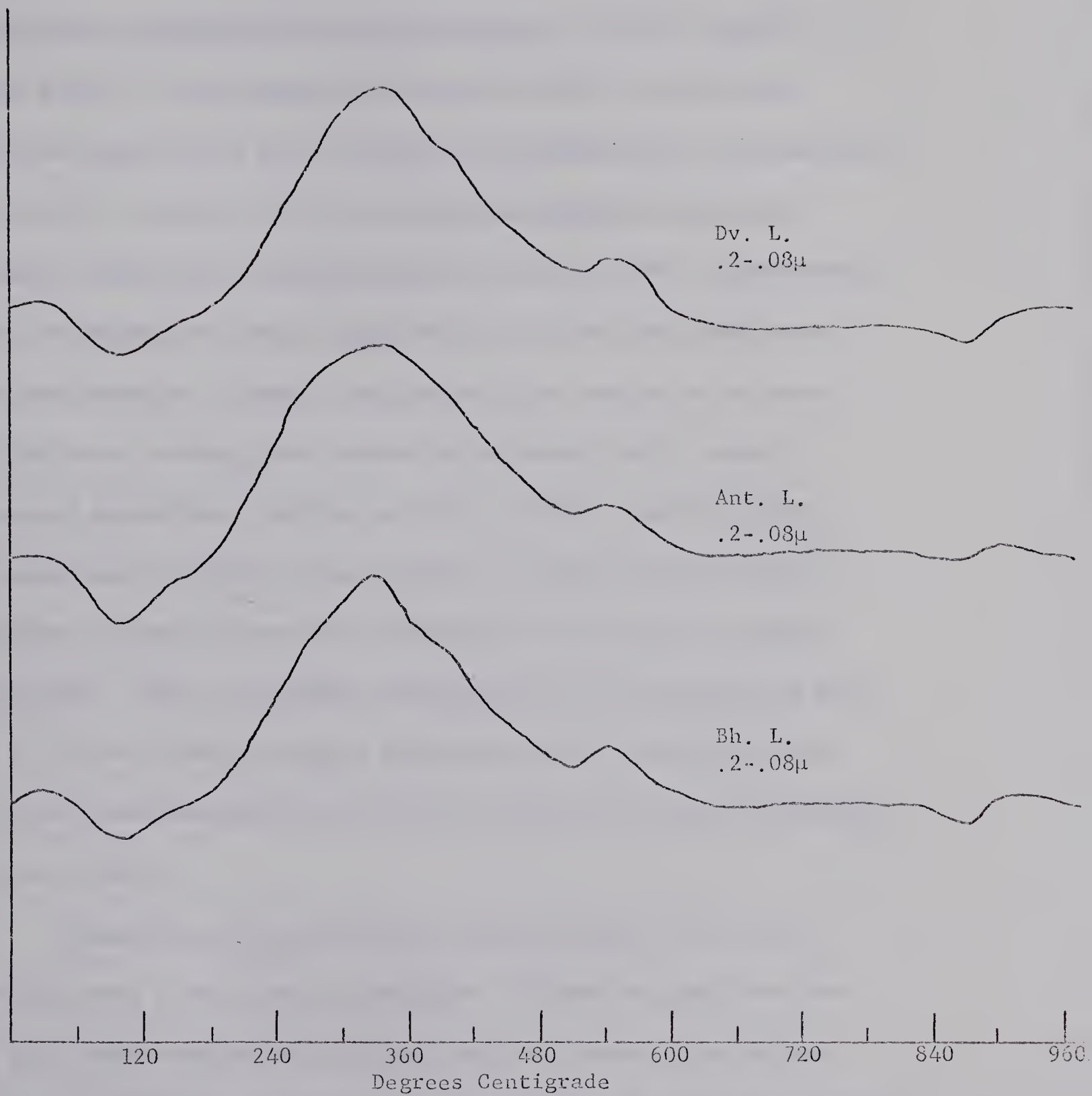


Figure 29 Differential thermographs of clay fractions separated from the Ah₂ horizon - untreated.

absent in the .2 - .08 micron fraction. Thus, three exothermic peaks are recognized in the thermographs: at 335° C, 440° C and 495° C. What appears to be a peak at 555° C is felt to be the net result of the 335° C exotherm accentuated by a OH endotherm at 510° C. Carthew (1955), working with piperidine saturated clays, found that the initial exothermic peak at 300° C represented the combustion of carbon deposited on the interlayer surfaces of montmorillonite. Similar conclusions were reached by Allaway (1948) who, working with piperidine-saturated clays, noted a marked exothermic reaction at 300° C - 350° C. In view of the conclusions reached by these authors, it appears that the 335° C exothermic peak represents combustion of interlayered organic material. This is somewhat substantiated by thermographs a and b in Figure 27 where organic interlayered clay was prepared by treating montmorillonite with lactose and ethylene glycol monoethyl ether (EGME).

Standard calcium-saturated montmorillonite was treated with lactose in an aqueous suspension, allowed to equilibrate for 4 days, then washed with distilled water to remove free lactose. Sufficient EGME was added to a second sample of calcium-saturated montmorillonite to form a paste. The clay was then placed in an oven at 60° C until dry. The differential thermographs of these samples indicate a strong 355° C exotherm.

Exothermic peaks and/or inflexions at temperatures greater than 335°C probably represent the combustion of free organic matter, the combustion of organic species expelled from the clay cells, and/or the stepwise pyrolysis and oxidation of organic molecules associated or unassociated with the clay minerals (Bodenheimer et al., 1966). That the latter suggestion is possible is substantiated by the differential thermal analysis of krilium and krilium-treated clays (Figure 27d, e and II).

NaOH- $\text{Na}_4\text{P}_2\text{O}_7$ treated clays. Differential thermographs of NaOH- $\text{Na}_4\text{P}_2\text{O}_7$ treated clays are shown in Figure 30. The effect of the chemical treatment has been to reduce or in some cases to eliminate the 440°C and 495°C exothermic peaks and inflexions. This chemical treatment has been widely used to remove free organic matter from soils (Kononova, 1966). The results of differential thermal analysis of NaOH- $\text{Na}_4\text{P}_2\text{O}_7$ treated clays suggest that the initial exothermic peak (between 290°C and 340°C) is due to combustion of complexed organic material, and the 440°C and 495°C exothermic peaks and inflexions were due to combustion of free organic matter.

If the foregoing discussion can be considered valid two important aspects of organo-clay complexes are evident. The results indicate that the fine clay fraction ($0.2 - .08\mu$) contains only complexed organic matter as evidenced by the absence of

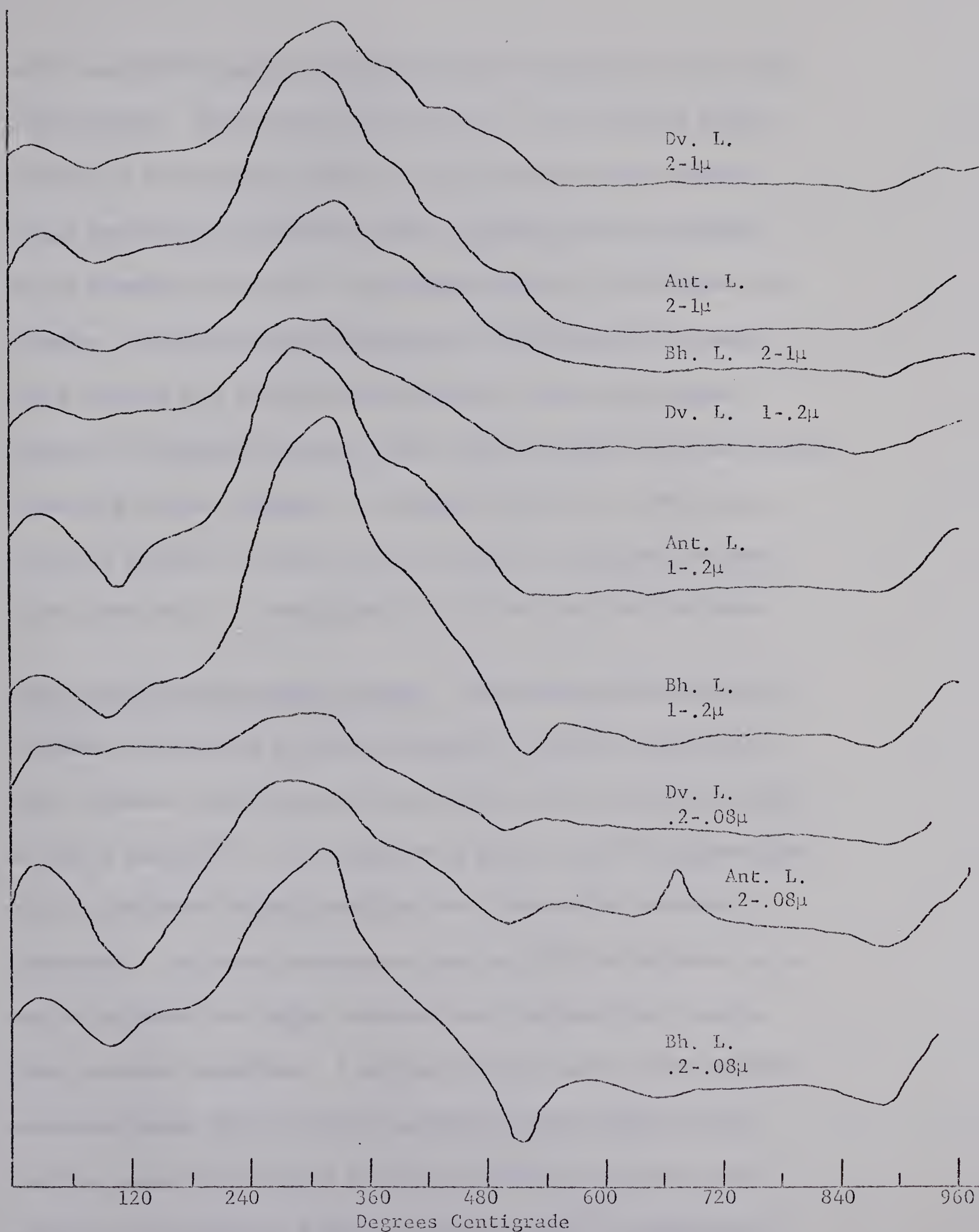


Figure 30 Differential thermographs of clay fractions separated from the Ah₂ horizon - NaOH-pyrophosphate treatment.

440° C and 495° C peaks in differential thermographs of untreated clay samples. The coarse clay fraction (2 - 1 μ) contains larger amounts of free organic matter, and at the same time contains larger amounts of complexed organic constituents as evidenced by the intensity of the 335° C exothermic peaks for untreated clay samples. Differential thermographs of NaOH-Na₄P₂O₇ treated clays indicate that Pincher Creek samples contain the lowest amount of complexed organic matter with Edmonton and Olds samples containing similar amounts. In addition, the 0.2 - 0.08 micron fractions appear to contain a lower content of complexed organic matter than the 2 - 1 micron and 1 - 0.2 micron size fractions.

Hydrogen peroxide treated samples. Differential thermographs of peroxide treated clay fractions (Figures 31 and 32) indicate that some residual carbon remained as evidenced by exothermic peaks at 320° C and 455° C. The exothermic peak at 320° C suggests that not all complexed organic material was removed by peroxide treatment. The sharp exothermic peak at 455° C is believed to be due to oxidation of a highly carbonaceous residue which results from peroxide treatment. A mixture of pure carbon with standard montmorillonite gave a similar exothermic peak (Figure 27C). Calcium oxalate which gave two sharp exothermic peaks at 446° C and 498° C also may be a likely cause of the 455° C exotherms in peroxide treated clays.

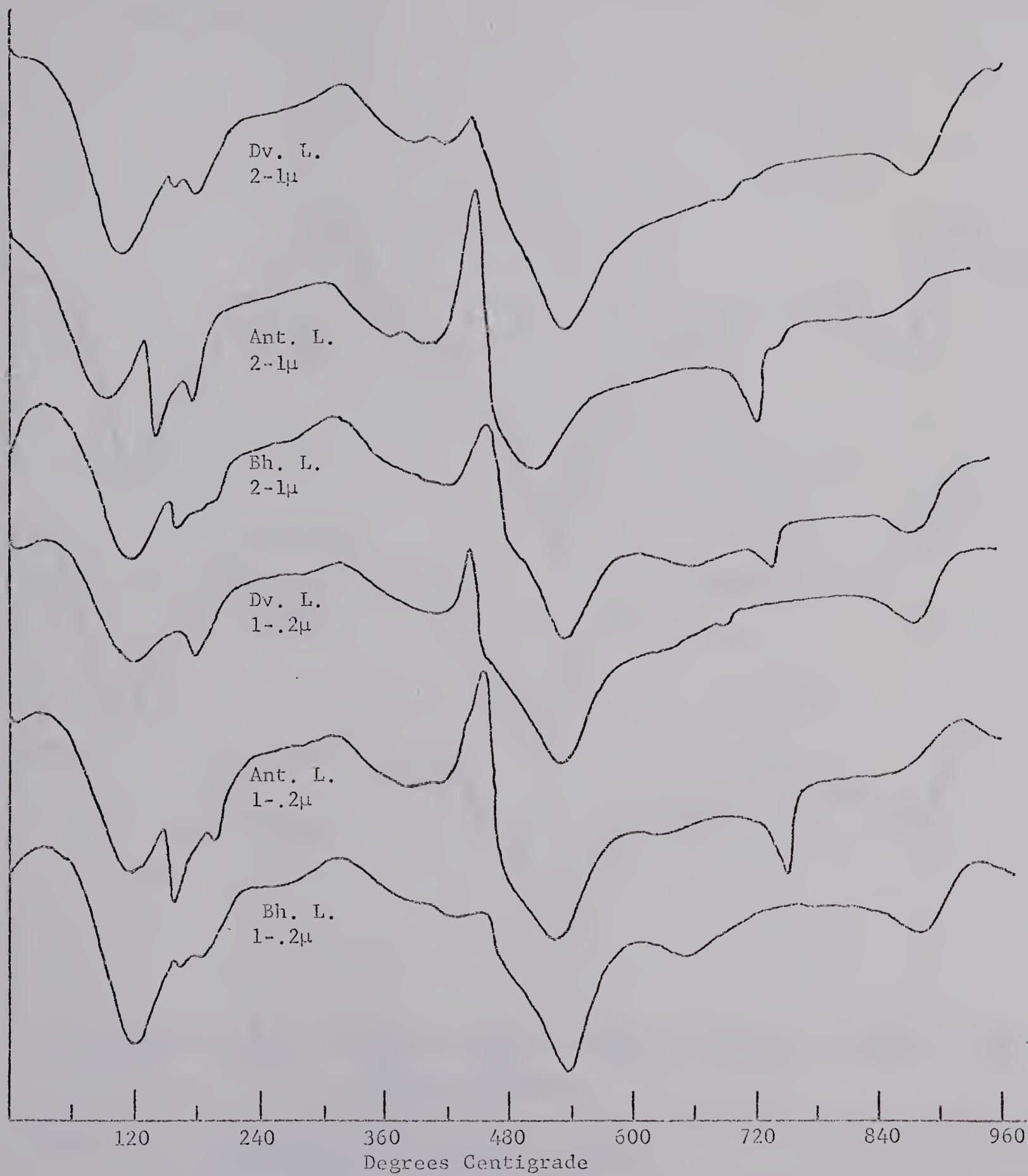


Figure 31 Differential thermographs of clay fractions separated from the Ah₂ horizon - peroxide treatment.

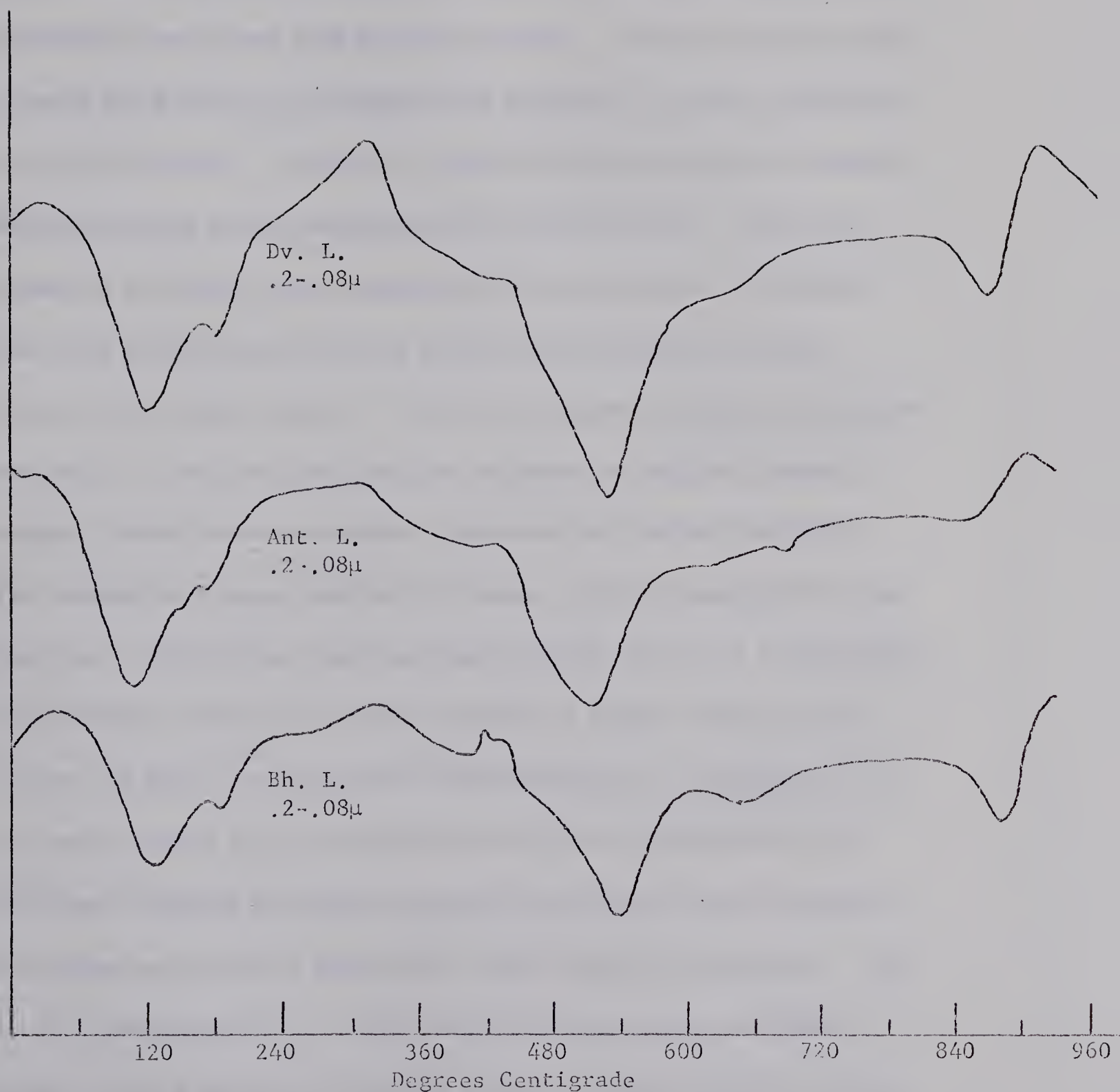


Figure 32 Differential thermographs of the clay fractions separated from the Ah₂ horizon - peroxide treatment.

Organic carbon content of the clay fractions. According to X-ray and differential thermal analysis, organic matter appears to be intimately associated with the clay fraction. Thermal analysis also reveals the presence of considerable amounts of organic matter in each clay fraction. In order to confirm these findings total carbon determinations were conducted on the clay fractions. Since the presence of CaCO_3 was not detected in Ah_2 horizons, it was felt that total carbon (as measured by the Leco induction furnace) represents organic carbon. The data as shown in Figure 33 indicate that the 2 - 1 micron clay fraction contains the largest amount of organic carbon before and after treatment with $\text{NaOH-Na}_4\text{P}_2\text{O}_7$. The content of organic carbon decreases with decreasing clay size fraction. Of the three clay fractions studied, the 0.2 - 0.08 micron clay fraction contains the lowest amount of organic carbon both before and after treatment with $\text{NaOH-Na}_4\text{P}_2\text{O}_7$. In addition, the untreated coarse clay fraction from the Olds and Edmonton Ah_2 horizons is higher in organic carbon than Pincher Creek samples. The same was found to apply after $\text{NaOH-Na}_4\text{P}_2\text{O}_7$ treatment. The 1 - 0.2 micron and 0.2 - 0.08 micron fractions does not differ greatly among the three sampling areas in organic carbon content before or after $\text{NaOH-Na}_4\text{P}_2\text{O}_7$ treatment.

The results for organic carbon content do not completely substantiate the results obtained for differential thermal analysis.

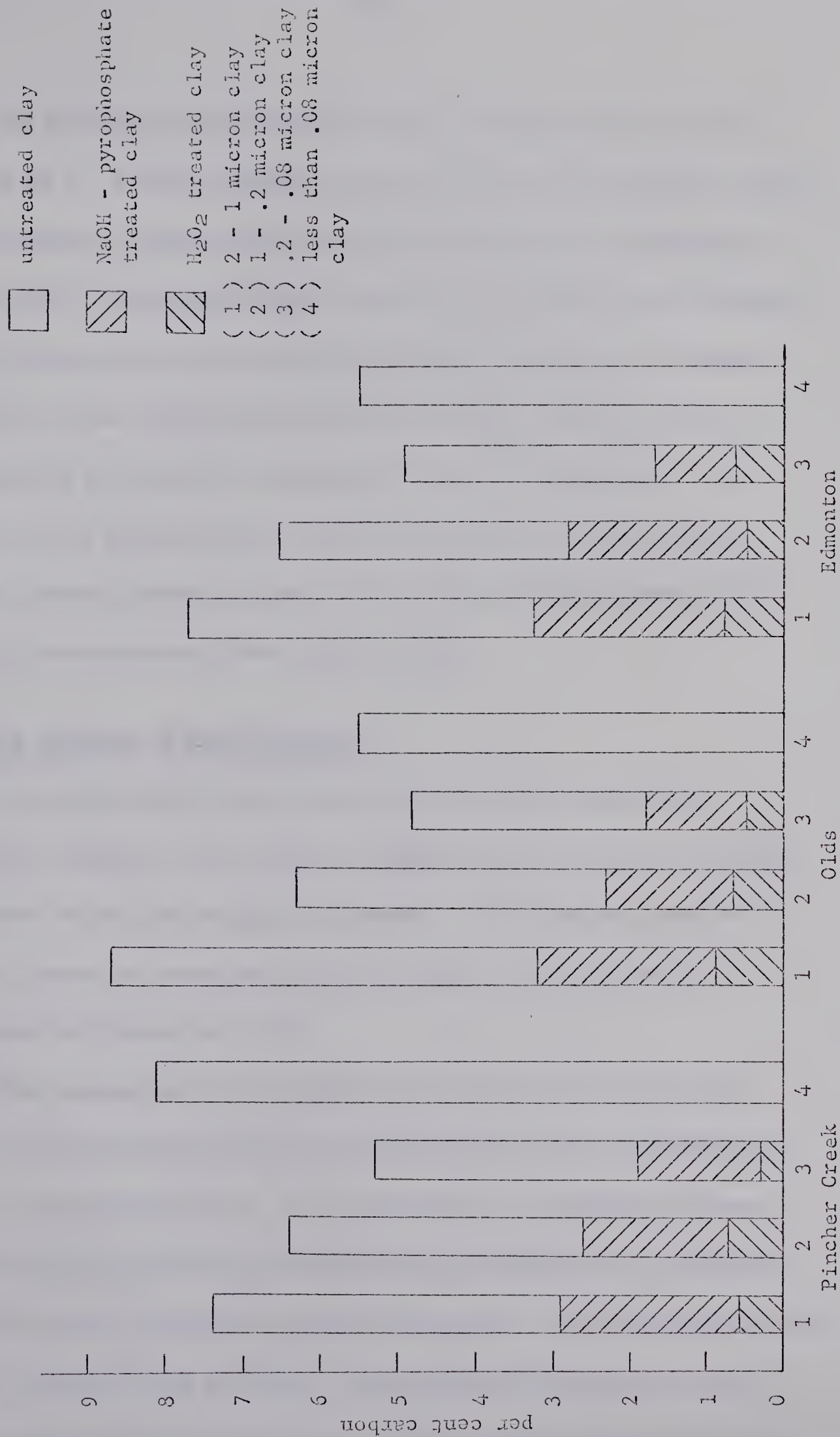


Figure 33 Total carbon content of Ah₂ clay fractions from the pooled Ah₂ horizons from the 3 major sampling areas. (Expressed as per cent of oven-dry weight.)

From the data shown in Figure 33 it can be seen that the fine clay fraction (0.2 - 0.08 μ) contains a large amount of free organic carbon. Interpretation of differential thermographs lead to the suggestion that the 335° C exothermic peak represents combustion of complexed organic matter and since no 440° C and 495° C peaks or inflexions occurred in fine clay fractions then all organic matter in the 0.2 - 0.08 micron fraction was complexed to the clay minerals. The validity of the interpretation of the thermographs and the data for organic carbon content largely rests on the assumption that NaOH-Na₄P₂O₇ removes only free organic matter.

Infrared Analysis of Clay Minerals

Infrared analysis was conducted on the clay samples to determine whether or not further evidence may be found to elucidate the nature of the clay-organo complexes. The infrared spectra of the clay fractions separated from the pooled Ah₂ horizons are presented in Figures 34 to 37.

The assignment of absorption frequency bands to functional groups of soil minerals has been approached by many investigators from an empirical fashion. A large number of samples have been studied and on the basis of similarities and differences, absorption bands have been assigned to certain vibrations. The infrared spectra of clay minerals such as illite, montmorillonite and chlorite have been extensively studied and most of the absorption bands have been

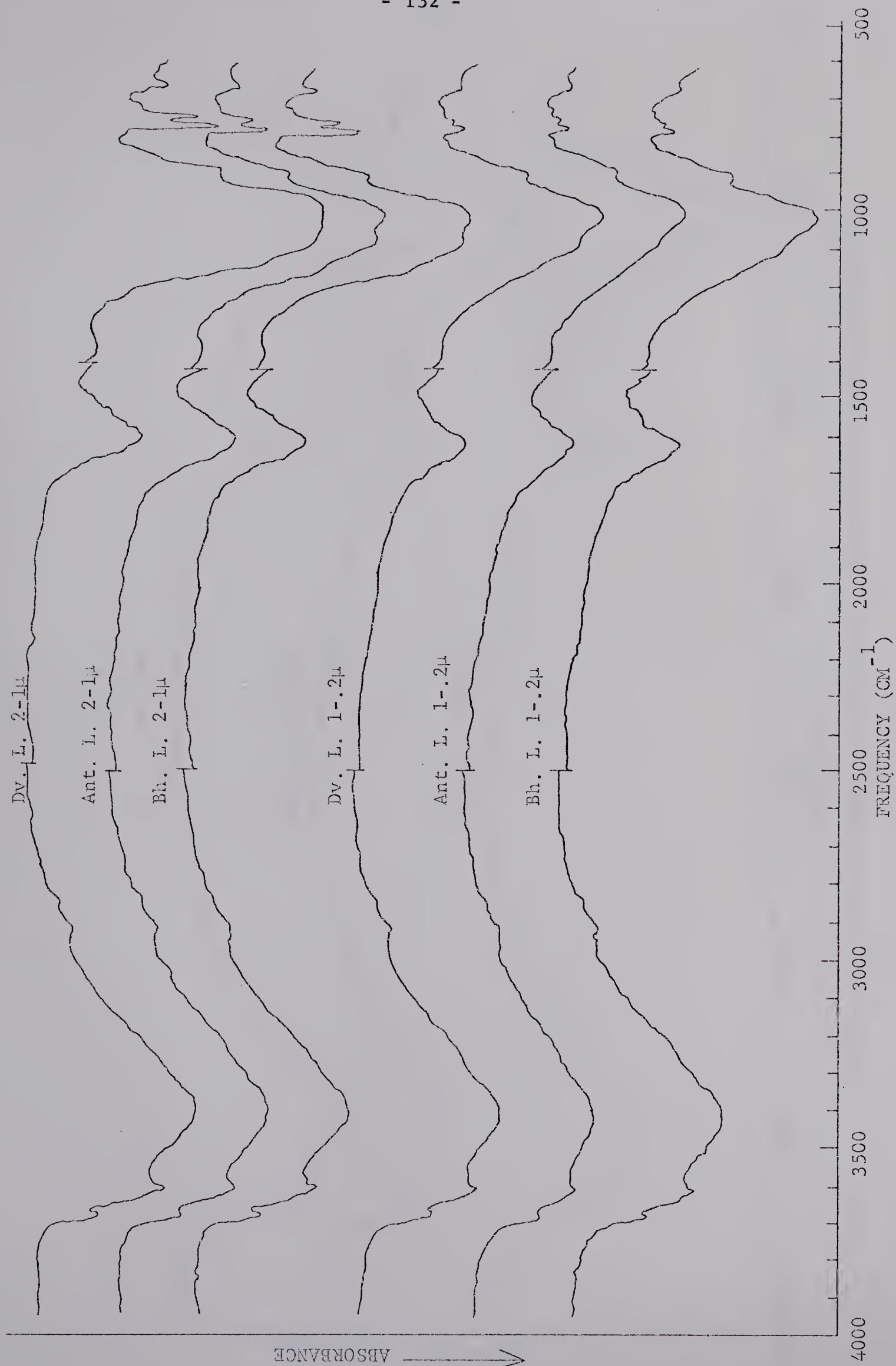


Figure 34 Infrared spectra of untreated clay fractions separated from the Ah₂ horizon.

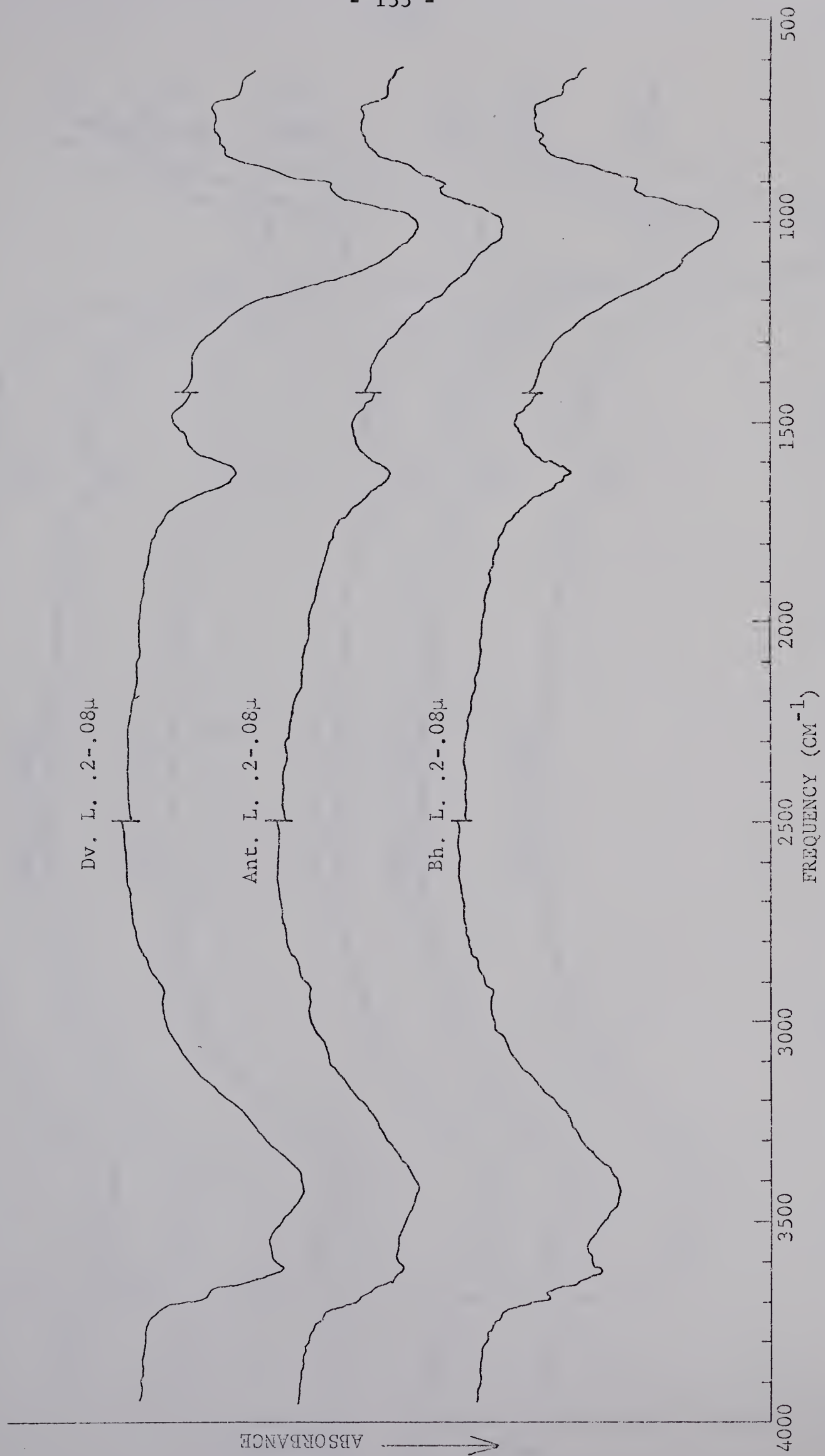


Figure 35 Infrared spectra of untreated clay fractions separated from the Ah₂ horizon.

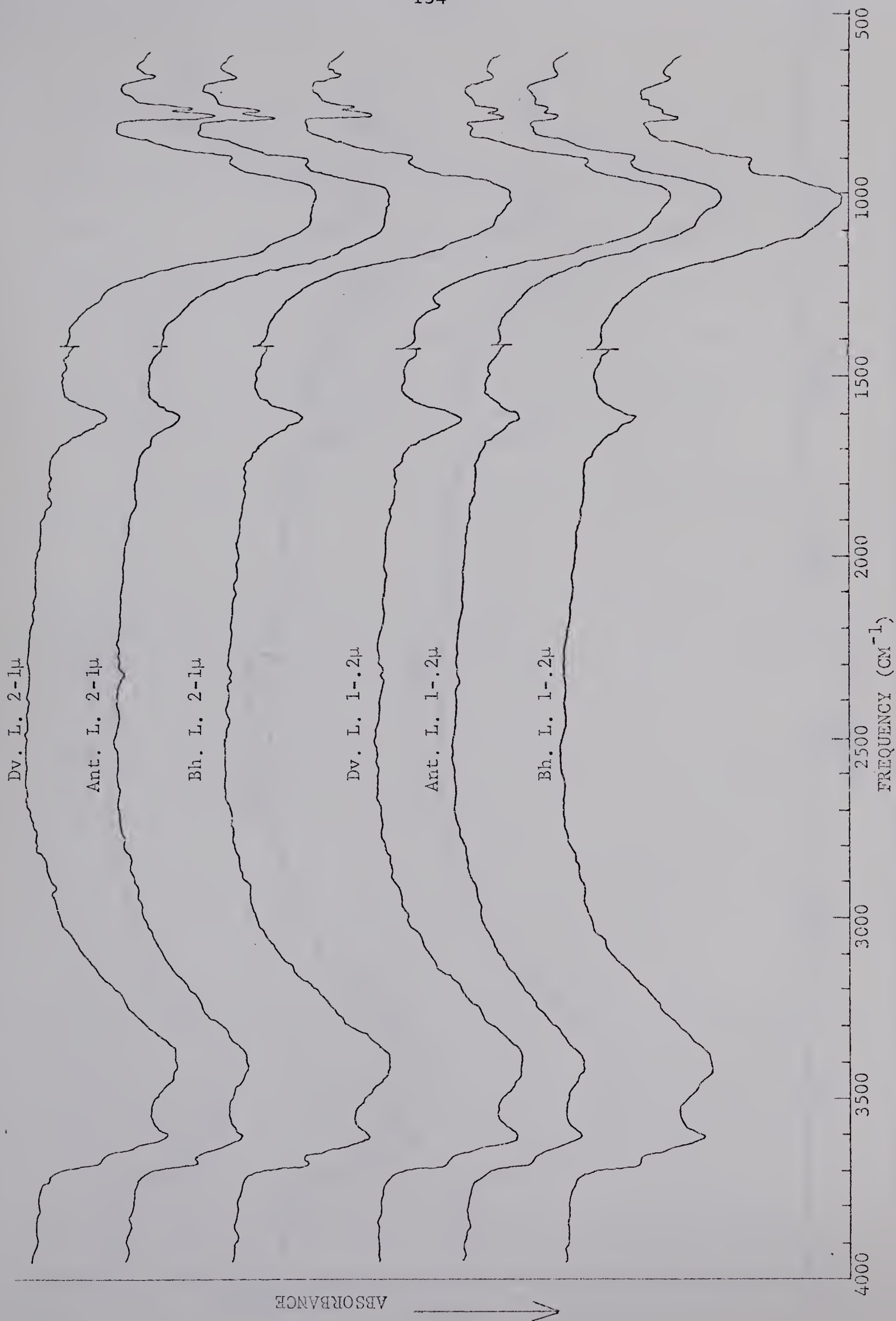


Figure 36 Infrared spectra of peroxide treated clay fractions from the Ah₂ horizon.

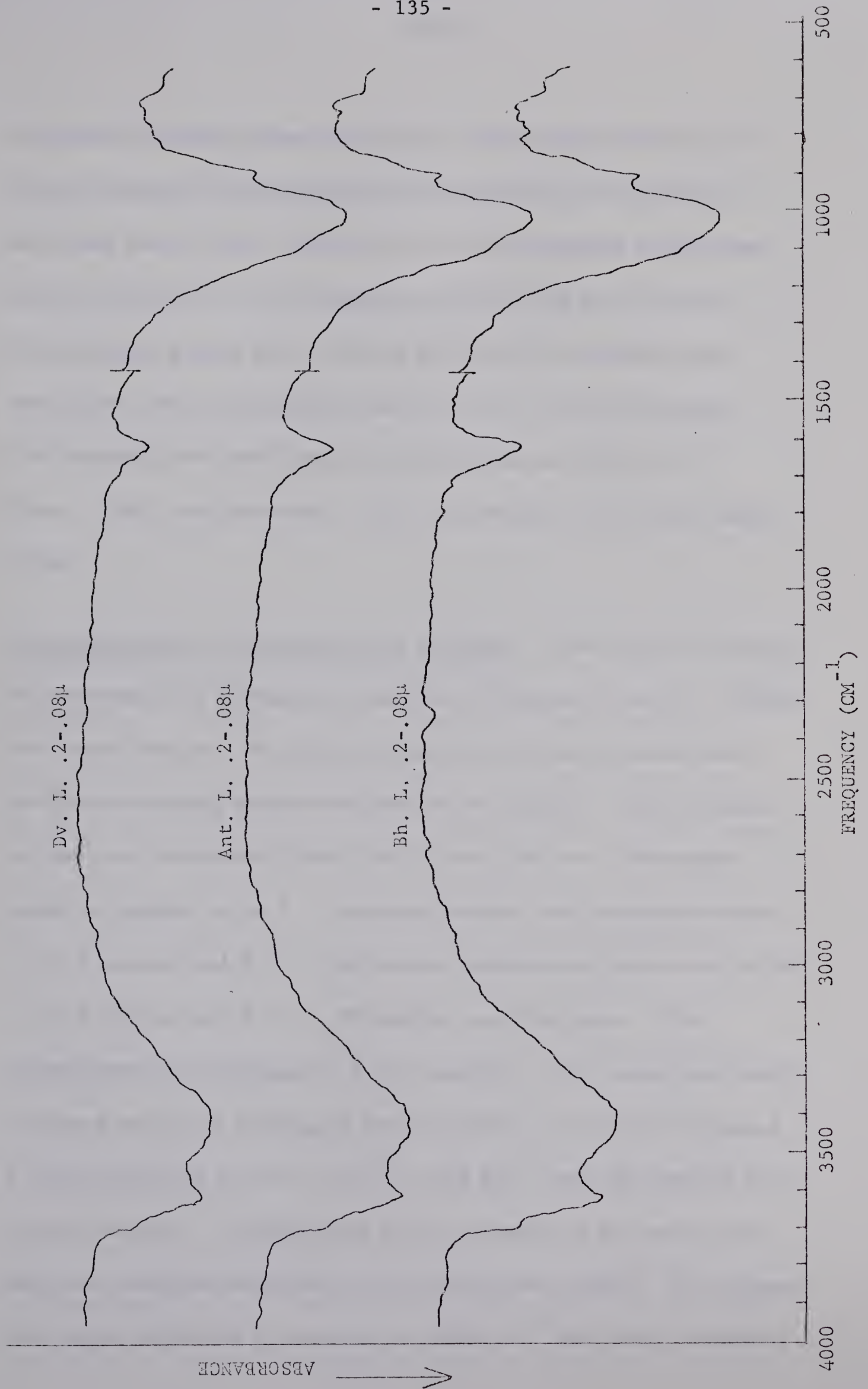


Figure 37 Infrared spectra of peroxide treated clay fractions separated from the Ah₂ horizon.

assigned to certain group vibrations. Main group vibrations of clays revealed by infrared analysis are hydroxyl stretching of adsorbed water ($3500 - 3100 \text{ cm}^{-1}$); H-O-H bending of adsorbed water (1630 cm^{-1}); Si-O vibrations ($1093 - 820 \text{ cm}^{-1}$); Si-O vibrations of quartz ($790, 770$ and 685 cm^{-1}); unbonded clay structural -OH stretch (3620 and 3700 cm^{-1}); clay structural -OH stretch (910 cm^{-1}) and O-Al-OH vibration (1120 cm^{-1}) (Kerr, 1950; van der Marel, 1961; Mortensen, 1965, and Little, 1966).

Infrared spectra of untreated clay fractions. The infrared spectra of untreated clay fractions are shown in Figures 34 and 35. Within each size fraction, the infrared spectrum for each sample from the three sampling areas was found to be similar. The presence of quartz as indicated by the $790, 770$ and 685 cm^{-1} absorption bands is highest in the $2 - 1$ micron fraction and decreases in the $1 - 0.2$ micron and $0.2 - 0.08$ micron fraction and decreases in the $1 - 0.2$ micron and $0.2 - 0.08$ micron size fractions. This substantiates the findings by X-ray analysis. The absorption band assigned to H-O-H bending of adsorbed water (1620 cm^{-1}) showed a slight decrease for Dv. L, Ant. L and Bh. L with decreasing size of clay fraction. No difference in the intensity of the peak among the three samples within each size fraction was noted. The intense absorption band with a maximum at 1020 cm^{-1} has been attributed

to a variety of Si-O vibrations. The broadening of the band to approximately 1070 to 1080 cm^{-1} was suggested to result from both Si-O vibrations and O-Al-OH vibrations. The relative intensity of this band is lowest for Olds samples. In addition the slope for the band (from 1300 cm^{-1} to 1100 cm^{-1}) is steepest in all fractions from the Pincher Creek samples. As the clay size fraction decreases the slope of the band also decreases. The weak absorption bands at 2850 and 2920 cm^{-1} indicate the presence of organic material, having aliphatic C-H groups, in the clay fraction. These two bands were noted in all fractions and samples occurring at approximately the same relative intensity. The 3400 cm^{-1} absorption band assigned to -OH stretching of adsorbed water has a greater intensity for Edmonton samples. As the clay size fraction decreases, the 3400 cm^{-1} also decreases in intensity. This trend, along with a similar decrease in the 1620 cm^{-1} absorption suggested a lower degree of hydration in the finer clay fractions. This lower degree of hydration may in reality be a reflection of a higher degree of adsorbed organic material. The 3610 cm^{-1} and 3680 to 3685 cm^{-1} absorption bands are attributed to stretching of free -OH groups attached to the octahedral layer. The 905 cm^{-1} to 910 cm^{-1} band is attributed to the stretching of structural -OH groups attached to dioctahedral layers. The general trend observed for the 3610 and 3685 cm^{-1} bands is a slight decrease in intensity as clay size

fraction decreased. In addition, these bands are least intense for the Olds samples. The relative decrease in intensity of the 3610 and 3685 cm^{-1} absorption bands is not as marked as the decrease in the 3400 cm^{-1} band which indicates a constancy in -OH group content.

Infrared spectra of peroxide treated clays. The effect of peroxide treatment on clays depicted by infrared analysis are shown by Figures 36 and 37. Several slight but significant differences are evident between untreated and peroxide-treated clays. Peroxide treatment resulted in a marked decrease in the 1620 cm^{-1} absorption band which is attributed to H-O-H bending of water. This suggests that the organic matter associated with the clay was hydrated or contained some H_2O molecules within its structure although the state of hydration of the clay may also be a factor. After peroxide treatment, clays were freeze-dried and analyzed; if a longer time was used to freeze-dry the clays, more adsorbed water could have been "stripped" off than in the original untreated sample. The 2920 and 2850 cm^{-1} absorption bands assigned to aliphatic C-H groups were not present in peroxide treated clays. The intensity of the 3610 cm^{-1} and 3685 to 3680 cm^{-1} increased as a result of peroxide treatment. In addition, a slight shift in the 3685 cm^{-1} band for untreated samples to 3680 cm^{-1} was caused by peroxide treatment. This evidence strongly suggests that organic matter

is complexed through the free -OH groups on the clay surfaces.

Peroxide treatment resulted in a marked change in the slope (between 1300 and 1100 cm^{-1}) of the main 1010 cm^{-1} absorption band. The removal of organic matter caused the slope of the infrared spectra in the 1300 cm^{-1} to 1100 cm^{-1} region to increase sharply when compared to untreated samples. Peroxide treatment also caused an increase in intensity of the 1010 cm^{-1} to 1020 cm^{-1} absorption band. The change in slope was greatest for the 1 - 0.2 micron and 0.2 - 0.08 micron fractions.

The changes in the infrared spectra of the clays resulting from peroxide treatment suggests an interaction between the organic and mineral fractions. The changes between peroxide treated and untreated samples were greatest for the finer clay fractions. The exact interaction of mineral and organic compounds and quantitative differences among samples were difficult to ascertain. The work of Tensmeyer et al. (1960) clearly showed that in the formation of montmorillonite-ketone complexes the infrared spectra of the organic compound was markedly changed but that of the montmorillonite was not. Tensmeyer suggested that organic-organic interaction is the main factor and the clay-organic interaction is the inducing factor in complex formation. In view of Tensmeyer's conclusions it is felt that the differences noted in the infrared spectra are minimal and inconclusive since it was the clay spectra under examination.

Cation Exchange Capacity of Clay Fractions

Cation exchange capacities for the clay fractions before and after peroxide treatment are shown in Table XI. The total C.E.C. for all untreated samples are similar in magnitude except for the Pincher Creek 0.2 - 0.08 micron fraction which is lower. After peroxide treatment of clays a trend appeared where total C.E.C. was found to increase with decreasing size fraction for samples from all three sampling areas. This trend was expected since finer clay size results in more broken edges which expose clay-OH groups capable of ionization at high pH values. Grim (1953) states that 80 per cent of the C.E.C. of montmorillonite was found to be due to isomorphous substitution within the octahedral layer. Since montmorillonite has a large portion of its C.E.C. as pH independent C.E.C., the observed increase in pH independent C.E.C. was attributed to the relative increase of montmorillonite in the finer clay fractions. The absolute values and trends for pH independent C.E.C. are in good agreement with the calculated values for montmorillonite content (Table X) in the various fractions. Observations for H₂O₂ treated samples showed an increase in pH dependent C.E.C. with a decrease in the clay size and was attributed to the contribution of exposed -OH groups in the finer clay fractions.

In general, the destruction of organic matter caused a decrease in the three types of C.E.C. determined (Table XII). However two

TABLE X. Cation Exchange Capacity of Clay Fractions

Separated from the Pooled Ah₂ Horizons for the Three Sampling Areas

Sampling area	Clay fraction	Total C.E.C.*		pH independent C.E.C.*		pH dependent C.E.C.*	
		Untreated	H ₂ O ₂ treated	Untreated	H ₂ O ₂ treated	Untreated	H ₂ O ₂ treated
Edmonton	2 - 1 μ	161.4	76.4	62.0	41.0	99.4	35.4
	1 - .2 μ	167.0	102.1	62.5	55.6	104.5	46.5
	.2 - .08 μ	157.8	134.2	70.8	76.7	87.0	57.5
Olds	2 - 1 μ	166.8	78.3	61.2	39.2	105.6	39.1
	1 - .2 μ	171.6	100.1	65.4	51.3	106.2	48.8
	.2 - .08 μ	167.9	119.1	64.5	63.1	103.4	56.0
Pincher Creek	2 - 1 μ	159.0	83.8	52.0	43.6	107.0	40.2
	1 - .2 μ	159.6	97.5	55.2	45.4	104.4	51.8
	.2 - .08 μ	132.0	118.1	74.8	74.8	57.2	43.3

* me./100 g untreated clay

TABLE XI. Effect of H_2O_2

Treatment on Cation Exchange Capacity

Sampling area	Clay fraction	Total C. E. C. *	pH independent C. E. C. *	pH independent C. E. C. *
Edmonton	2 -1 μ	-85.0	-21.0	-64.0
	1 - .2 μ	-64.9	- 6.9	-58.0
	.2- .08 μ	-23.6	+ 5.9	-29.5
Olds	2 -1 μ	-88.5	-22.0	-66.5
	1 - .2 μ	-71.5	-14.1	-57.4
	.2- .08 μ	-48.8	- 1.4	-47.4
Pincher Creek	2 -1 μ	-75.2	- 8.4	-66.8
	1 - .2 μ	-62.1	- 9.8	-52.6
	.2- .08 μ	-13.9	0	-13.9

* me./100 g untreated clay

- indicates a decrease

+ indicates an increase

effects of organic matter on C.E.C. in the clay systems were evident. The first was a contributive effect where the presence of organic matter increased the exchange capacity as a result of its own exchange-absorption capacity. On a unit weight basis, soil organic matter has a much higher cation exchange capacity than clay minerals. Secondly, organic matter complexed to the clay blocked exchange sites on the clay thereby reducing the measured exchange capacity. It is likely that both effects of organic compounds were operative in the clay-organic systems under investigation.

After peroxide treatment, the total C.E.C. decreased markedly indicating that a substantial portion of the total C.E.C. was the result of the presence of soil organic materials. The magnitude of the difference decreased with a reduction in particle size. A similar trend was noted for total carbon content where a decrease occurred with a decrease in clay size. Comparing the total carbon contents and the decrease in total C.E.C. (resulting from peroxide treatment) for the various samples, it was observed that the decrease in total C.E.C. for the 0.2 - 0.08 micron clay size fraction was much smaller than would be expected from the decrease in total carbon content. Since large qualitative differences were not evident in the type of organic material associated with the different clay fractions, it is suggested that the exchange-adsorption

groups of organic constituents (probably hydroxyls) in the fine clay fraction were unavailable during the exchange capacity determinations for untreated clays. However another contributing factor may also have resulted from the involvement of clay hydroxyl groups in complex formation in the 0.2 - 0.08 micron fraction where they could not contribute to the measured C.E.C. After peroxide treatment, the total exchange capacity determined for the fine clay decreased only slightly. The loss of the exchange capacity due to removal of organic matter was largely compensated for by the release and availability of clay exchange sites which initially were unavailable because of bonding with organic material. On this basis the data suggested greatest complexing in the 0.2 - 0.08 micron clay size fraction. Within this clay size fraction, the Pincher Creek sample had the greatest degree of clay-organo complexing followed by Edmonton, then Olds samples.

Organic matter was generally found to increase the pH independent cation exchange capacity. Theoretically, organic matter should have little or no influence on the pH independent C.E.C. Although organic matter functional groups should not ionize at pH 3.0, it is conceivable that by using KCl at a concentration of 2 normal some exchange of H^+ from functional groups could result. Physical adsorption of K^+ may also have occurred.

The effect of organic matter removal on pH dependent C.E.C. (calculated by difference) indicated a similar trend as total C.E.C. It is likely that the same factors that influence the total C.E.C. also influence pH dependent C.E.C.

Electron Microscopic Examination of Clays

Electron micrographs of clays treated with humic acid (Plate 10) showed that humic acid was entirely adsorbed by montmorillonite. In addition, the adsorbed humic acid formed linkages between clay particles. No indication was evident that finer clay particles were more involved in adsorbing humic acid. However, the system used was far from being indicative of natural conditions.

The general appearance of soil organic materials associated with clay mineral particles (Plates 11 to 14) suggested a similarity to the water extractable organic matter viewed in Plate 8. Often, the organic material has a netted, opaque appearance although in some cases (Plate 12, photograph 3; Plate 14, photograph 2) the organic material is characterized by the presence of light gray tones and a conspicuous absence of the netted appearance. Uncomplexed clay minerals may be observed in shades of dark gray to black on the photographs.

The electron micrographs of untreated clays (Plates 11 to 14) suggest that the largest quantities of organic material are associated with the fine clay fraction. This is especially true of

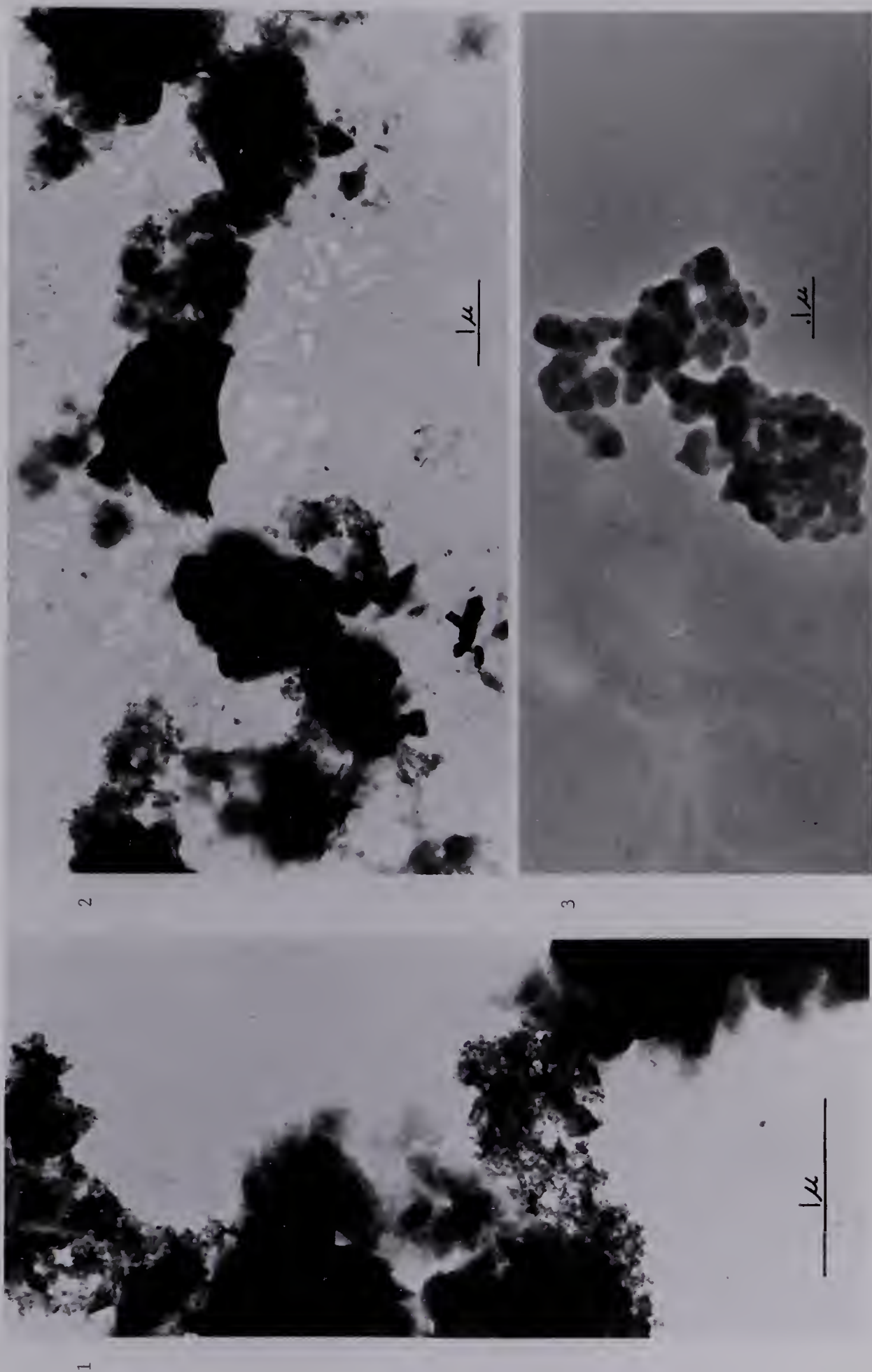


Plate 10 Electron micrographs of clay-humic acid complexes.

Description of Plate 10

- Photograph 1. Electron micrograph of calcium saturated montmorillonite after addition of 5% humic acid. The humic acid, appearing "spongy-granular", occurs as bridges between the montmorillonite particles.
- Photograph 2. Electron micrograph of calcium saturated montmorillonite treated with humic acid obtained from the Olds Ah₂ horizons. Humic acid is shown to be bound to the montmorillonite particles.
- Photograph 3. Electron micrograph showing "shot-like" material resulting from peroxide treatment of clays.

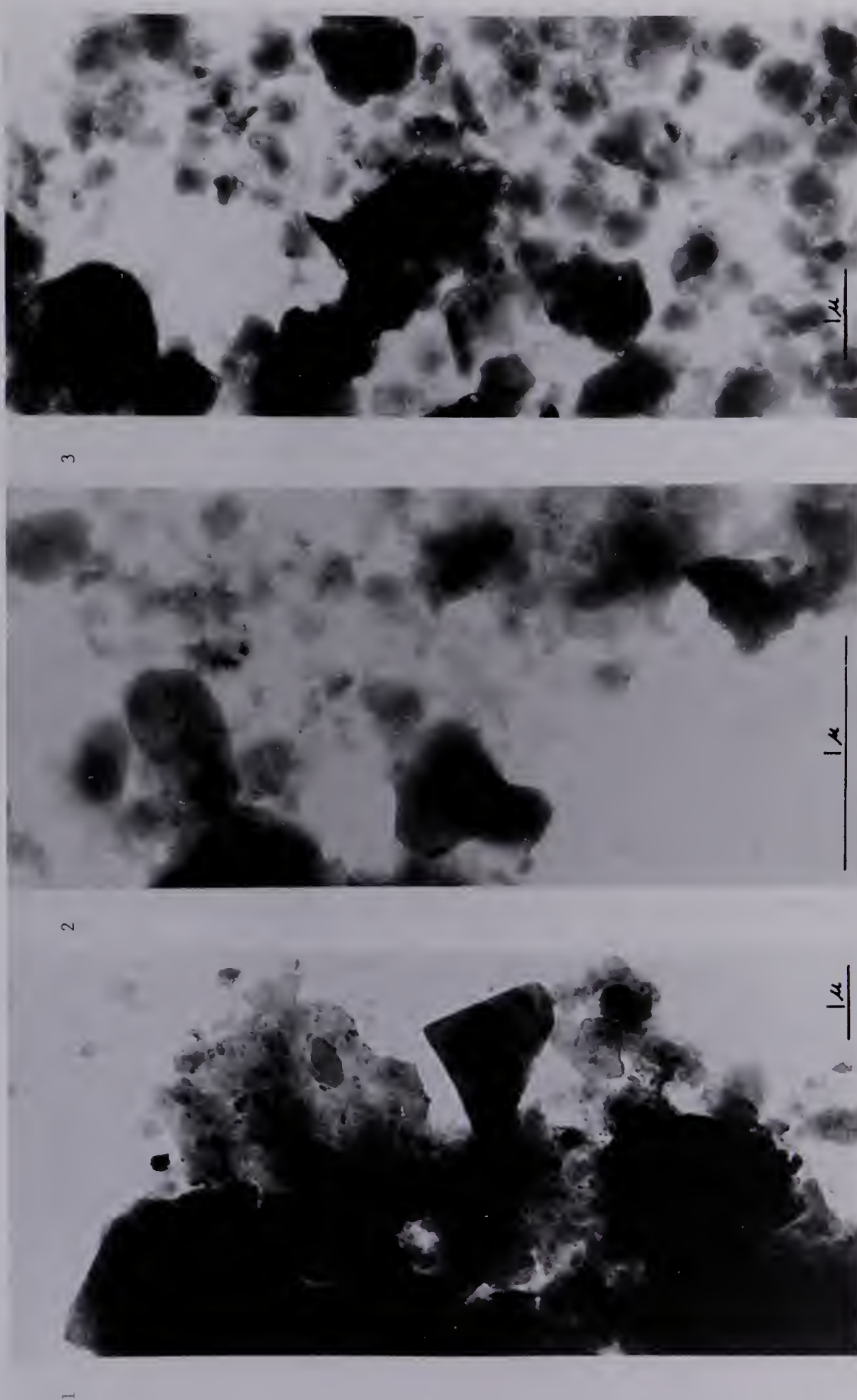


Plate 11 Electron micrographs of the total clay fraction separated from the pooled Ah₂ horizons - no treatment.

Description of Plate 11

- Photograph 1. Electromicrograph of the total clay fraction separated from pooled Ah₂ horizons sampled in the Edmonton area.
- Photograph 2. Electron micrograph of the total clay fraction separated from the pooled Ah₂ horizons sampled at Olds. Adsorbed organic matter is seen on the surface and edges of clay particles. The organic fraction has a mottled or netted appearance on the photograph.
- Photograph 3. Electron micrograph of the total clay fraction separated from the pooled Ah₂ horizons sampled at Pincher Creek. The clay minerals are seen to be intimately associated with organic compounds. The organic material appears as opaque globules surrounding and on the surfaces of clay particles.

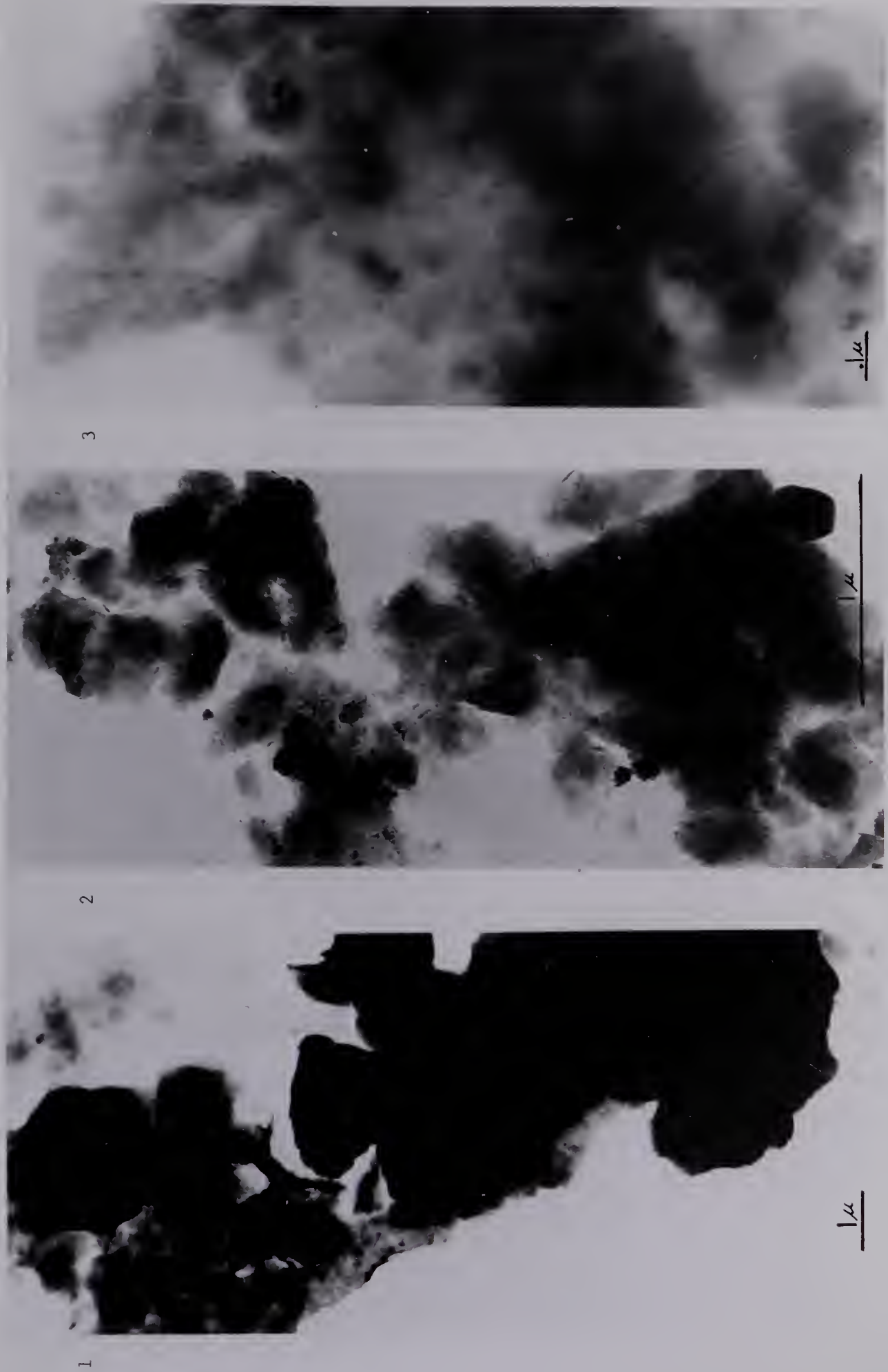


Plate 12 Electron micrographs of untreated clay fractions separated from the pooled Ah₂ horizons - Edmonton area.

Description of Plate 12

- Photograph 1. Electron micrograph of the 2 - 1 micron clay fraction. The scale indicates that particles larger than 2 microns were obtained in the separation procedure. The preparation of the sample for photographing may have caused some aggregation of the clay particles. Very little organic matter is observed in this micrograph.
- Photograph 2. Electron micrograph of the 1 - 0.2 micron clay fraction. The ill-defined boundary or edges of some clay minerals suggests the possibility of complexed organic matter.
- Photograph 3. Electron micrograph of the 0.2 - 0.08 micron clay fraction. The material photographed appears to be predominantly organic in nature.

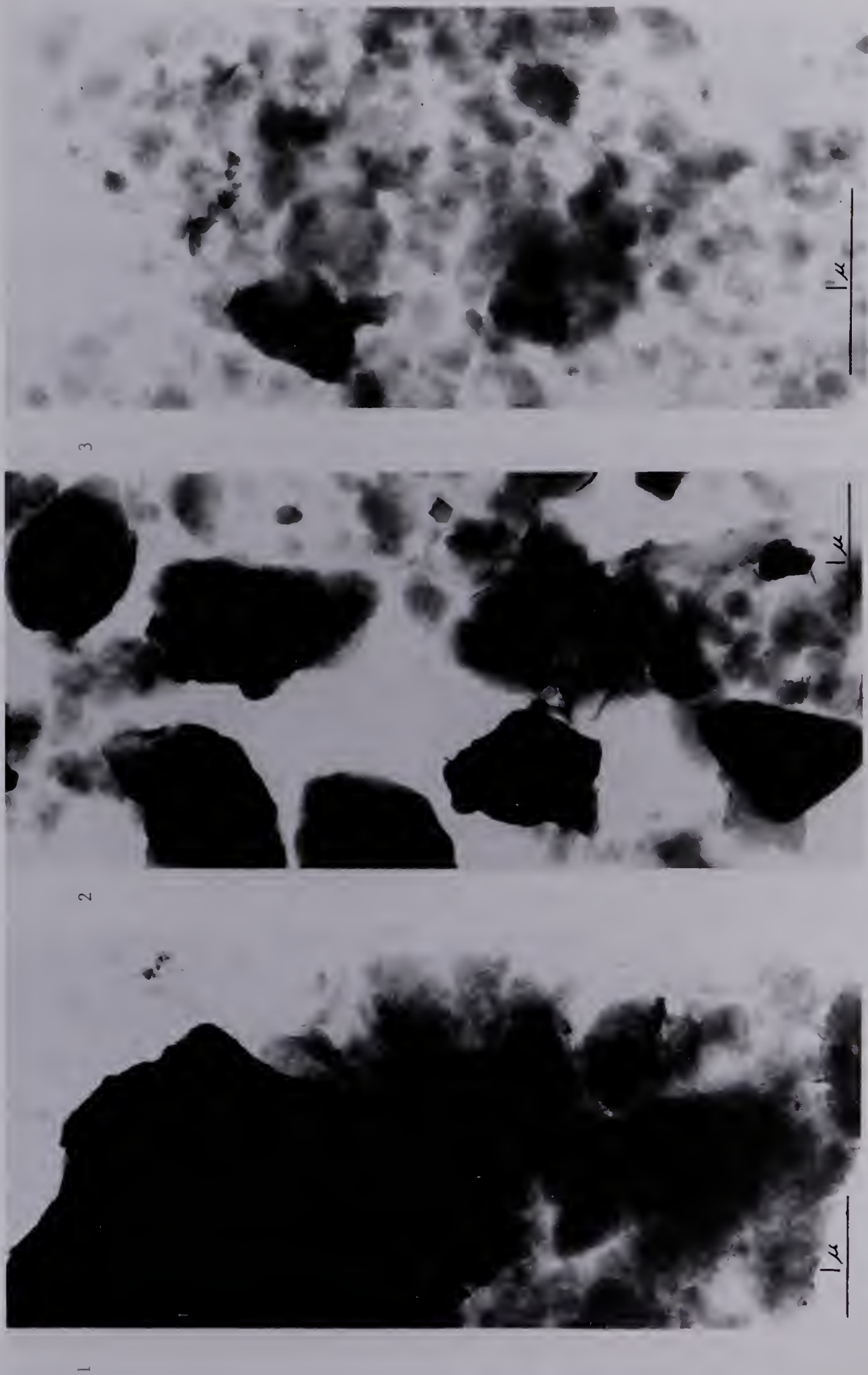


Plate 13 Electron micrographs of untreated clay fractions separated from the pooled Ah horizons - Olds area.

Description of Plate 13

- Photograph 1. Electron micrograph of the 2 - 1 micron clay fraction. The diffuse edges are typical of montmorillonite.
- Photograph 2. Electron micrograph of the 1 - 0.2 micron clay fraction. The edges of many of the clay minerals appear diffuse; this appearance could be due to montmorillonite and/or adsorbed organic matter.
- Photograph 3. Electron micrograph of the 0.2 - 0.08 micron clay fraction. The opaque appearance of the particles suggest thin layers of minerals or organic matter.

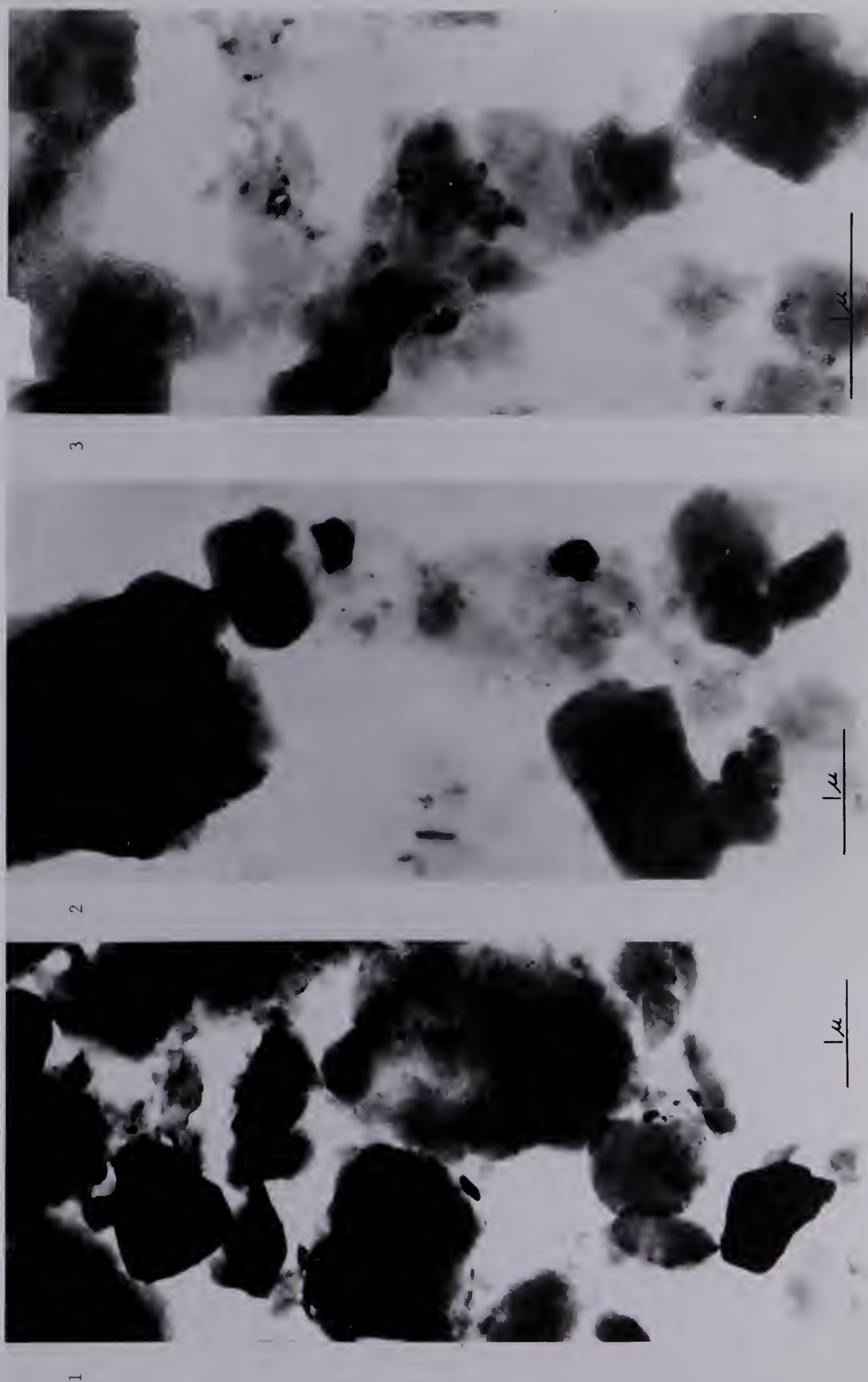


Plate 14 Electron micrographs of untreated clay fractions separated from the pooled Ah₂ horizons - Pincher Creek area.

Description of Plate 14

- Photograph 1. Electron micrograph of the 2 - 1 micron clay fraction. Surfaces of clay minerals are relatively "clean".
- Photograph 2. Electron micrograph of the 1 - 0.2 micron clay fraction. Organic material similar to that shown in Plate 8, photograph 3 can be seen surrounding the finer clay particles in the middle of the photograph.
- Photograph 3. Electron micrograph of the 0.2 - 0.08 micron clay fraction. Very good evidence of complexed organo-clay compounds appear in this electron micrograph. The organic material, having a "netted" appearance engulfs and links clay particles.

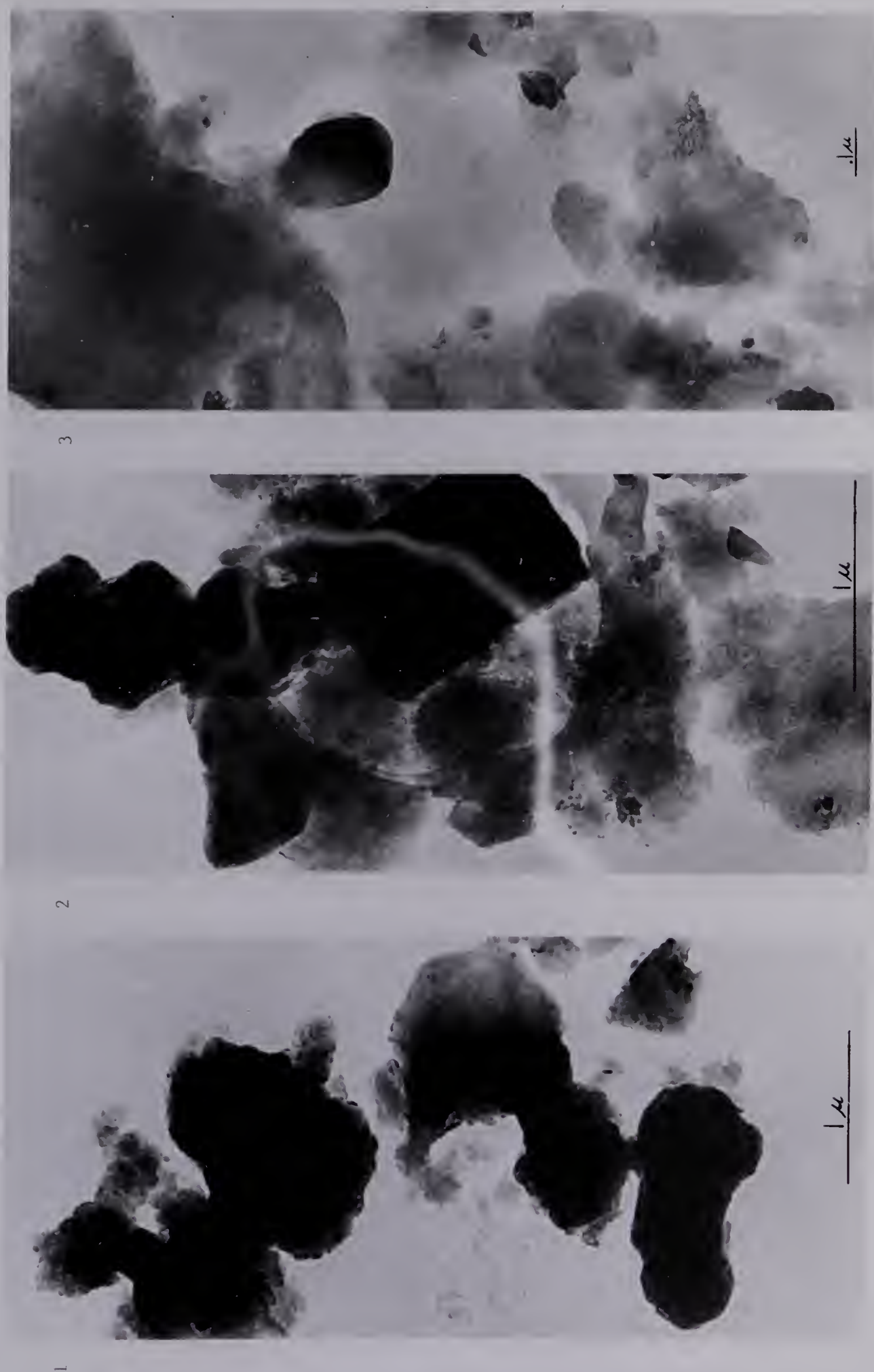


Plate 15 Electron micrographs of H_2O_2 treated clay fractions separated from the pooled Ah_2 horizons - Edmonton area.

Description of Plate 15

- Photograph 1. Electron micrograph of the peroxide treated
2 - 1 micron clay fraction. The surfaces and
edges of the clay minerals are well-defined
and no evidence of organic matter is present.
- Photograph 2. Electron micrograph of the peroxide treated
1 - 0.2 micron clay fraction.
- Photograph 3. Electron micrograph of the 0.2 - 0.08 micron
clay fraction.

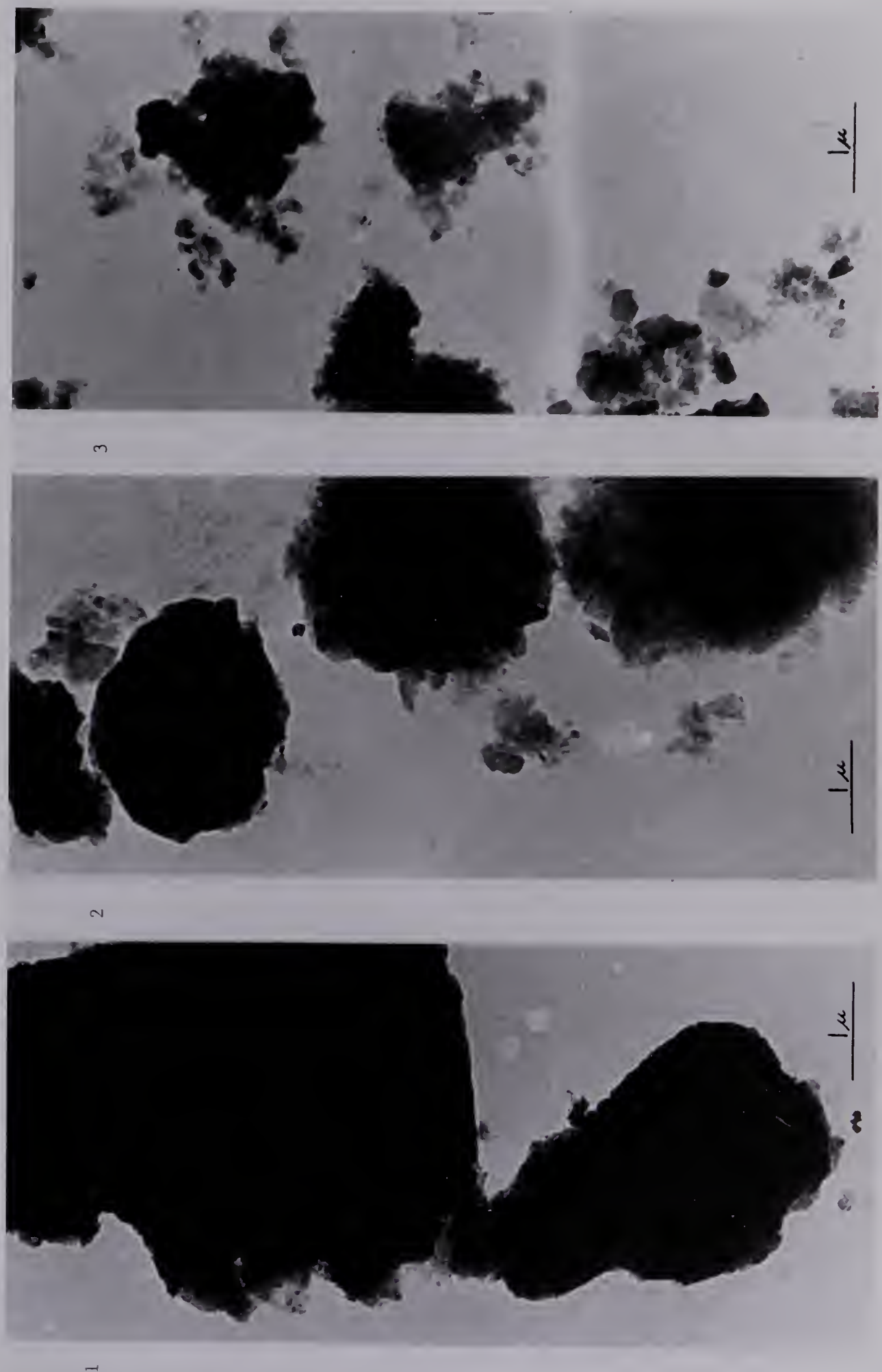


Plate 16 Electron micrographs of H_2O_2 treated clay fractions separated from the pooled Ah_2 horizons - Olds area.

Description of Plate 16

- Photograph 1. Electron micrograph of the 2 - 1 micron clay fraction after peroxide treatment. The edges are well-defined, the particles are similar in appearance to illite and chlorite.
- Photograph 2. Electron micrograph of the 1 - 0.2 micron clay after H_2O_2 treatment.
- Photograph 3. Electron micrograph of the 0.2 - 0.08 micron clay fraction.

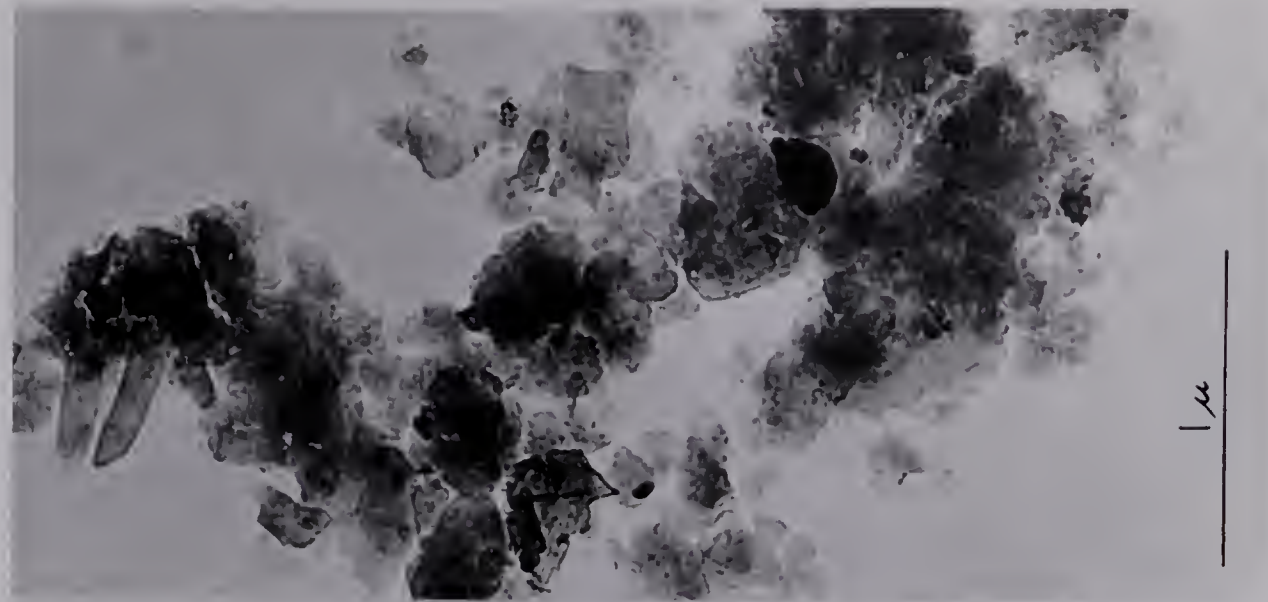
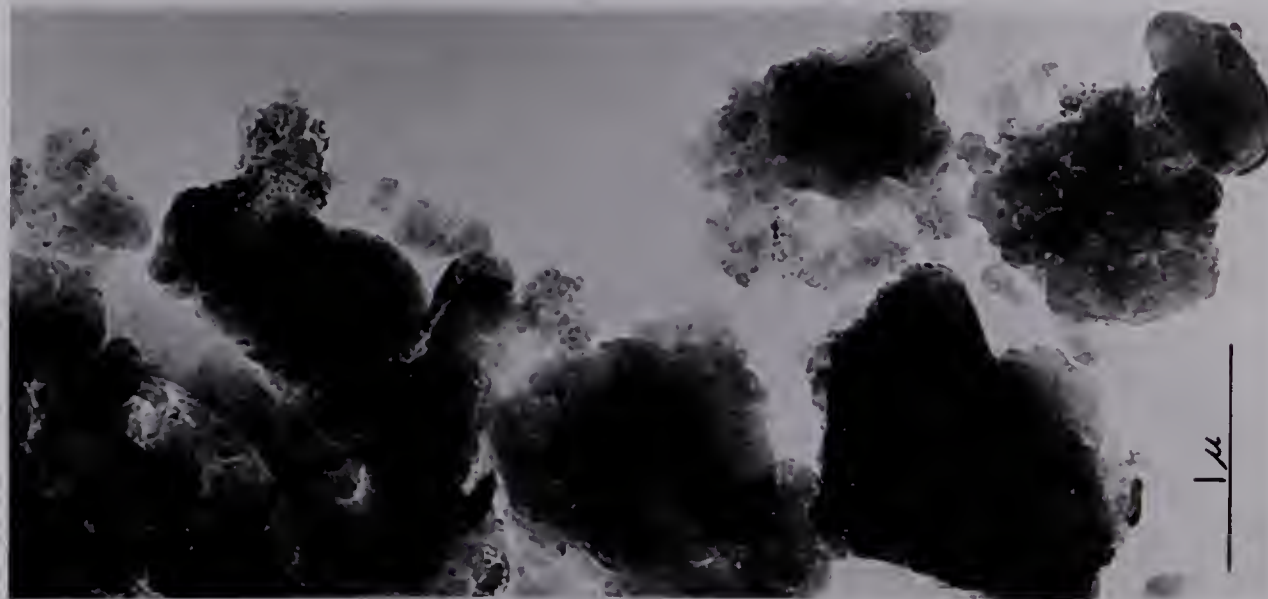


Plate 17 Electron micrographs of H_2O_2 treated clay fractions separated from the pooled Ah_2 horizons - Pincher Creek area.

Description of Plate 17

- Photograph 1. Electron micrograph of the 2 - 1 micron clay fraction after peroxide treatment. The well-defined edges indicate illite or chlorite.
- Photograph 2. Electron micrograph of the 1 - 0.2 micron clay fraction after peroxide treatment. Tiny granules scattered throughout well-defined clay minerals are evident.
- Photograph 3. Electron micrograph of the 0.2 - 0.08 micron clay fraction after peroxide treatment. The edges of the minerals are quite well-defined and no organic materials are evident. Tiny granules forming clusters are scattered throughout the minerals.

the Pincher Creek sample (Plate 11, photograph 3) where a large portion of the fine clay fraction is engulfed by organic material. Plates 12 to 14 also show similar trends. The 2 - 1 micron clay fractions are almost free of adsorbed organic material as indicated by the well-defined edges and dark tones of clay minerals. This indicates that much of the organic matter detected by D. T. A. and total carbon determination in the coarse clay fraction occurs as uncomplexed organic matter and was not photographed.

After peroxide treatment, the clay minerals showed no signs of organic materials as recognized in the untreated samples. Tonal differences between sample material and the formvar support are sharp and particle boundaries are well-defined. Electron micrographs of peroxide treated samples show tiny granules which occurred individually or in clusters. Plate 10, photograph 3 is a high power magnification of one such cluster. These granules, resulting from peroxide treatment, are probably calcium oxalate. The differential thermographs also suggest the presence of calcium oxalate in peroxide treated clay samples.

V. SUMMARY AND CONCLUSIONS

Ah horizons in the southern portion of the Chernozemic belt were described as "soft" and "fluffy" while Ah horizons in the central and northern area of the Chernozemic belt were described as having "stronger" structure. Examination of thin sections showed that the microstructure of Ah horizons from the Pincher Creek area are different from the microstructure of Ah horizons from the Edmonton and Olds areas. The microstructure of Pincher Creek Ah horizons consisted of spherical granules of plasmic material varying from 0.1 to 0.4 mm in diameter. Mineral grains were found to be unbound. The microstructure of Ah horizons from the Edmonton and Olds sites consisted of irregularly shaped granules 0.2 to 1 mm and occasionally greater in diameter with mineral grains embedded in a porous groundmass of plasmic material. The thin sections confirmed the field observations.

Analysis of the polysaccharide and polyuronide content of Ah and B horizons showed that Pincher Creek soils have higher contents than Edmonton and Olds soils. No significant differences in contents were found between Olds and Edmonton samples. A larger portion of total carbon as polysaccharide and polyuronide carbon was found for Pincher Creek soils. Edmonton and Olds samples were similar in this regard. This indicated that a

qualitative and quantitative difference in the soil organic matter exists between Pincher Creek soils and those of the Edmonton and Olds areas.

Functional group analysis of humic acid extracted from pooled Ah₂ horizons indicated that samples from the Olds area have the highest exchange-adsorption capacity. The Edmonton sample was lowest in total functional group content with the Pincher Creek sample being intermediate. The same trend was found for phenolic hydroxyl groups. Humic acid extracted from the Olds soils was found to contain the highest content of carboxyl groups. The content of carboxyl groups was lowest in humic acid extracted from Pincher Creek soils; the Edmonton sample was found to have an intermediate content.

Infrared analysis of humic acid samples substantiated the results obtained for functional group analysis. The infrared spectra suggested humic acid from Pincher Creek Ah₂ horizons was of lower molecular weight and more aliphatic in nature. Electron micrographs of the three humic acid samples showed some variation but this may have been the result of technique in sample preparation. However the general appearance of the three humic acid samples was found to be typical of those reported for chernozemic humic acid.

Analysis of the humic acid fraction also suggested a difference in the organic matter composition of soils at the three locations.

The qualitative and quantitative analyses suggested humic acid from Pincher Creek soils was of lower molecular weight. Olds and Edmonton humic acid samples were found to be similar in this regard. On these bases, it may be concluded that humic acid from Olds and Edmonton soils are more complex and mature in nature.

The clay mineral suite of C horizons was found to be similar for all sites studied. In general, the dominant clay mineral in the C horizons was found to be montmorillonite which comprised approximately two-thirds of the clay fraction. Illite was found to account for 20 per cent of the clay mineral content. Olds samples were found to contain a slightly higher content of chlorite and/or kaolinite. From the mineralogical data it may be concluded that the parent materials in the three sampling areas are similar.

Chemical and physical analyses of total clay separated from the B horizons indicated similarity among samples. The general features associated with the mineralogy of B horizons relative to C horizons were:

- (a) presence of some organic matter as indicated by exothermic peaks in differential thermographs;
- (b) indication of interlamellar penetration of organic matter in montmorillonite and/or weathering of illite as evidenced by broadening of the 17 Å peak;

- (c) in situ development and/or translocation of clay in the B horizons as evidenced by higher montmorillonite content, field observations of Btj horizons and mechanical analysis.

From these features it was concluded that the clay fraction of B horizons had undergone small but significant changes as a result of pedogenic processes.

Chemical and mineralogical characteristics of clay fractions separated from pooled Ah₂ horizons were studied in order to determine the nature and degree of clay-organic matter complex formation. Clays were separated into the 2 - 1, 1 - 0.2 and 0.2 - 0.08 micron fractions and studied using D. T. A. , X-ray, C. E. C. , organic carbon content, electron microscopic and infrared analysis.

Differential thermal and infrared analysis showed that organic matter is intimately associated with all clay fractions. There was good agreement between results obtained by D. T. A. and total organic carbon content. The coarse clay fraction (2 - 1 micron) was shown to have the largest amount of total organic carbon associated with it. Differential thermal analysis also indicated that some of the organic carbon occurs in interlamellar positions. X-ray analysis also suggested this possibility. Following peroxide treatment, the analytical data suggested that some residual organic matter still remained complexed to clay minerals and was not

completely removed.

Cation exchange capacity of untreated and peroxide treated clays was conducted to provide further information on clay-organo complexing. It was found that the magnitude of the difference for total C.E.C. between untreated and peroxide treated clay fractions decreased with decreasing clay size fraction. Although distribution of organic carbon content suggested that a decrease in total C.E.C. should have occurred, the difference encountered for the 0.2 - 0.08 micron fraction was much less than predicted from the total organic carbon content. On the basis of this data it was concluded that the 0.2 - 0.08 micron clay fraction exhibited the largest degree of clay-organo complexing. Further evidence provided by electron micrographs and infrared analysis also suggested that larger amounts of complexed organic occurred in the fine clay fraction. Visual evidence of clay-organo complexes was presented in the electron micrographs.

From the chemical and mineralogical analysis of clays separated from Ah₂ horizons it was concluded that the 0.2 - 0.08 micron clay fraction was most active in clay-organo complexing. The clay fractions separated from Pincher Creek soils showed the greatest degree of complexing between clay and organic fractions, followed by Edmonton samples with Olds samples showing the least amount of complexing.

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and Wright, 1959)

APPENDIX

TABLE Ia. Conversion Table for Degrees 2Θ
to d-spacing in Angstrom Units (for $\text{CuK}\alpha$ Radiation)

Degrees 2Θ	d-spacing A	Degrees 2Θ	d-spacing A
2.0	44.2	16.0	5.5
2.5	35.3	16.5	5.4
3.0	29.4	17.0	5.2
3.5	25.2	17.5	5.1
4.0	22.1	18.0	4.9
4.5	19.6	18.5	4.8
5.0	17.7	19.0	4.7
5.5	16.1	19.5	4.6
6.0	14.7	20.0	4.4
6.5	13.6	20.5	4.3
7.0	12.6	21.0	4.2
7.5	11.8	21.5	4.1
8.0	11.0	22.0	4.0
8.5	10.4	22.5	4.0
9.0	9.8	23.0	3.9
9.5	9.3	23.5	3.8
10.0	8.8	24.0	3.7
10.5	8.4	24.5	3.6
11.0	8.0	25.0	3.6
11.5	7.7	25.5	3.5
12.0	7.4	26.0	3.4
12.5	7.1	26.5	3.4
13.0	6.8	27.0	3.3
13.5	6.6	27.5	3.2
14.0	6.3	28.0	3.2
14.5	6.1	28.5	3.1
15.0	5.9	29.0	3.1
15.5	5.7	29.5	3.0

TABLE IIa. Some Chemical and Physical

Site no.	Hor- izon	Depth (in.)	pH	%N	%C	CaCO ₃ %	C/N	Exchangeable cations**				
								H ⁺ *	Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺
1	Ah ₁	0- 6	6.9	.47	5.39	ND	11.5	1.1	0.1	1.1	23.6	2.0
	Ah ₂	6-12	6.7	.31	3.54	ND	11.4	1.2	0.1	1.0	18.2	1.8
	Bm	12-24	6.5	.10	0.84	ND	8.4	0.9	0.1	0.5	13.9	2.8
	C _k	+24	7.5	ND	ND	4.20	ND	ND	0.1	0.5	21.5	5.1
2	Ah ₁	0- 5	6.7	.61	6.55	ND	10.7	1.7	0.1	0.8	26.9	0.7
	Ah ₂	5- 9	6.4	.37	4.29	ND	11.6	2.1	0.1	0.5	21.9	1.7
	Bm	9-19	6.3	.14	1.32	ND	9.4	0.9	0.1	0.4	16.9	1.1
	C _k	+19	7.5	ND	ND	6.23	ND	ND	0.1	0.3	31.5	0.7
3	Ah ₁	0- 6	6.4	.62	6.98	ND	11.2	2.7	ND	0.9	28.6	1.2
	Ah ₂	6-16	6.3	.27	3.27	ND	12.1	2.3	0.1	0.3	20.4	3.2
	Bm	16-28	5.9	.07	0.77	ND	11.0	1.5	0.2	0.3	16.5	4.0
	C	+28	6.2	ND	ND	ND	ND	1.1	0.3	0.3	15.9	3.7
4	Ah ₁	0- 8	6.2	.56	6.64	ND	11.8	2.6	ND	2.3	24.0	2.6
	Ah ₂	8-15	5.8	.35	4.01	ND	11.4	2.7	ND	0.1	20.8	0.6
	Bm	15-26	6.2	.08	0.97	ND	12.1	1.1	0.1	0.5	14.1	2.1
	C _k	+26	7.6	ND	ND	7.14	ND	ND	ND	ND	ND	ND

* Exchange Acidity

** me. / 100 g

Analyses of the Soils in the Edmonton Area

Total C. E. C.		Mechanical analyses					
Sum of Ex. Cat. me. / 100 g	Deter- mined	Sand %	Silt %	Clay %	Fine clay %	Fe ₂ O ₃ %	Al ₂ O ₃ %
27.9	31.4	34	44	22	14	0.04	0.05
22.3	25.2	38	41	21	14	0.04	0.06
18.2	20.7	38	39	23	17	0.04	0.04
27.2	14.0	42	38	20	14	0.03	0.03
30.2	37.7	33	43	24	17	0.04	0.06
26.3	30.0	33	39	28	18	0.07	0.07
19.4	22.3	23	48	29	18	0.10	0.09
32.6	16.2	35	41	24	15	0.04	0.03
33.4	39.9	22	48	30	18	0.04	0.06
26.3	28.9	23	46	31	20	0.05	0.06
22.5	24.9	27	38	35	21	0.03	0.05
21.3	24.0	19	51	30	18	0.05	0.08
31.5	35.7	36	36	28	17	0.04	0.07
24.2	29.8	35	37	28	17	0.05	0.09
17.9	20.0	42	36	22	16	0.05	0.03
ND	ND	42	36	22	13	0.04	0.06

TABLE IIIa. Some Chemical and Physical Analyses

Site no.	Horizon	Depth (in.)	pH	%N	%C	CaCO ₃ %	C/N	Exchangeable cations**				
								H ⁺ *	Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺
1	Ah ₁	0- 5	7.0	.60	8.61	ND	14.4	7.8	0.1	0.2	32.2	1.4
	Ah ₂	5-16	6.9	.31	3.92	ND	12.6	1.8	0.1	0.2	25.9	1.7
	Bm	16-23	7.4	.06	0.61	1.07	10.2	ND	0.1	0.3	16.0	2.3
	Cca	+23	7.7	ND		6.28	ND	ND	ND	ND	ND	ND
2	Ah ₁	0- 6	6.3	.64	8.12	ND	12.7	12.3	0.1	0.7	29.2	0.0
	Ah ₂	6-17	6.0	.36	4.53	ND	12.6	12.7	0.1	0.5	19.7	1.6
	Bm	17-30	5.9	.07	0.61	ND	8.7	2.3	0.2	0.4	13.6	1.8
	Cca	+30	7.4	ND	ND	8.27	ND	ND	0.1	0.3	34.8	0.0
3	Ah ₁	0-14	6.6	.51	6.68	ND	13.1	8.6	0.1	0.4	29.4	0.4
	Ah ₂	14-19	6.3	.25	3.32	ND	13.3	7.8	0.1	0.4	21.2	0.0
	Bm	19-28	5.9	.06	0.54	ND	9.0	1.9	0.1	0.4	14.1	0.6
	Cca	+28	7.7	ND	ND	18.76	ND	ND	ND	ND	ND	ND
4	Ah ₁	0- 8	7.6	.45	6.27	ND	13.9	ND	0.3	0.4	36.9	ND
	Ah ₂	8-15	7.8	.23	2.76	.64	12.0	ND	0.1	0.3	25.9	ND
	Bm	15-24	7.7	.06	0.52	.64	8.7	ND	0.1	0.5	17.5	0.5
	Cca	+24	7.9	ND	ND	29.00	ND	ND	0.2	0.1	29.8	ND

* Exchange Acidity

** me./100 g

of the Soils in the Olds Area

Total C.E.C.		Mechanical analyses					
Sum of Ex. Cat. me. / 100 g	Deter- mined	Sand %	Silt %	Clay %	Fine clay %	Fe ₂ O ₃ %	Al ₂ O ₃ %
41.7	47.6	28	49	23	16	.08	.06
29.7	33.4	29	44	27	15	.08	.10
18.7	20.4	37	40	23	14	.05	.07
ND	ND	60	15	25	12	.05	.03
42.3	40.4	22	60	18	11	.10	.08
34.6	29.3	30	48	22	13	.12	.09
18.3	18.9	31	42	27	16	.06	.05
35.2	16.4	40	35	25	14	.04	.02
38.9	38.9	25	49	26	14	.13	.05
29.5	27.8	24	50	26	14	.12	.05
17.1	19.1	38	37	25	17	.07	.03
ND	ND	35	49	16	6	.03	.01
37.6	33.3	33	50	17	9	.05	.02
26.3	23.5	32	51	17	6	.05	.03
18.6	16.4	32	39	29	21	.05	.02
30.1	6.5	37	50	13	10	.02	.01

TABLE IVa. Some Chemical and Physical Analyses

Site no.	Hor- izon	Depth (in.)	pH	%N	%C	CaCO ₃ %	C/N	Exchangeable cations**				
								H ⁺ *	Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺
1	Ah ₁	0- 4	6.1	.77	9.98	ND	12.9	3.5	.1	0.9	31.7	10.7
	Ah ₂	4- 9	6.0	.24	5.05	ND	20.2	3.3	.03	0.5	25.3	8.3
	Btj ₁	9-17	5.8	.18	2.08	ND	11.8	2.3	.05	0.5	18.4	4.8
	Btj ₂	17-29	6.3	.09	1.07	ND	11.6	0.7	.05	0.5	22.8	6.8
	Cca	29-39	7.4	ND	ND	18.19	ND	ND	.80	0.1	5.7	1.9
	C _k	+39	7.7	ND	ND	17.32	ND	ND	.90	0.1	4.4	1.9
2	Ah ₁	0- 6	6.3	.46	6.03	ND	13.1	8.6	.20	0.4	23.2	0.8
	Ah ₂	6-10	6.0	.35	3.93	ND	11.2	2.8	ND	0.7	20.4	0.7
	Bm-Btj	10-23	6.3	.12	1.20	ND	10.0	1.6	ND	0.5	21.6	3.3
	Cca	+23	7.4	ND	ND	13.63	ND	ND	.1	0.4	35.4	0.1
3	Ah ₁	0- 5	6.1	.66	7.42	ND	11.2	14.2	ND	1.2	26.2	0.2
	Ah ₂	5-14	6.1	.50	5.14	ND	10.3	10.9	.1	0.7	24.0	0.0
	Btj	14-27	6.1	.10	1.07	ND	10.7	1.8	.1	0.4	16.0	2.4
	Cca	+27	7.3	ND	ND	11.43	ND	ND	.1	0.4	37.6	0.0
4	Ah ₁	0- 5	6.1	.59	6.33	ND	10.7	10.1	ND	1.6	24.3	0.0
	Ah ₂	5-11	6.1	.32	3.67	ND	11.5	2.7	ND	0.9	18.8	0.4
	Bm	11-24	6.3	.09	1.00	ND	11.1	1.7	.1	0.6	18.7	1.7
	Cca	+24	7.5	ND	ND	13.15	ND	ND	.1	0.4	39.6	0.0

* Exchange Acidity

** me. / 100 g

of the Soils in the Pincher Creek Area

Total C.E.C.

Sum of Ex. Cat. me./100 g	Deter- mined	Mechanical analyses				Fe ₂ O ₃ %	Al ₂ O ₃ %
		Sand %	Silt %	Clay %	Fine clay %		
46.9	46.4	25	46	29	14	ND	ND
37.4	35.6	27	33	40	25	ND	ND
26.0	25.4	26	36	38	25	ND	ND
30.6	26.9	20	44	37	21	ND	ND
ND	15.4	32	33	35	17	ND	ND
ND	ND	35	35	30	16	ND	ND
33.2	32.9	38	30	32	19	.08	.09
24.6	29.5	35	32	33	21	.08	.09
27.0	26.0	29	36	35	18	.03	.06
36.0	19.9	28	41	31	15	.02	.03
41.8	37.1	37	30	33	17	.08	.09
35.7	33.7	39	31	30	19	.08	.09
20.7	22.3	38	30	32	17	.03	.07
38.1	21.4	23	38	39	19	.02	.04
36.0	34.9	45	28	27	15	.07	.07
22.8	27.4	44	29	27	18	.07	.06
22.8	25.1	35	32	33	20	.03	.06
40.1	22.6	38	34	38	19	.02	.04

TABLE Va. Munsell Renotations of Samples
from Chernozemic Black Ah₁ and Ah₂ Horizons

Munsell Renotation								
Sample*	Hue	Air-dry		Chroma	Hue	Field capacity		Chroma
		Value	Value			Value	Value	
Ah ₂ PC 1	0.85 Y	2.8		1.3	9.7 YR	1.8		1.3
Ah ₁ PC 1	9.65 YR	2.55		1.15	9.95 YR	1.7		1.1
Ah ₂ PC 2	0.75 Y	3.1		1.35	0.4 Y	1.9		1.3
Ah ₁ PC 2	0.4 Y	2.65		1.15	9.4 YR	1.8		1.2
Ah ₂ PC 3	0.2 Y	3.1		1.6	9.8 Y	2.1		1.6
Ah ₁ PC 3	0.25 Y	2.55		1.15	9.8 YR	1.9		1.4
Ah ₂ PC 4	0.45 Y	3.2		1.6	0.1 Y	2.2		1.8
Ah ₁ PC 4	0.35 Y	2.65		1.1	9.7 YR	1.9		1.4
Ah ₂ O 1	9.97 YR	3.0		1.2	0.2 Y	2.1		1.3
Ah ₁ O 1	10.0 YR	2.75		1.05	0.4 Y	1.5		0.8
Ah ₂ O 2	0.4 Y	2.9		1.3	0.6 Y	1.5		1.1
Ah ₁ O 2	0.8 Y	2.95		1.15	0.5 Y	1.6		0.9
Ah ₂ O 3	0.15 Y	2.85		1.2	9.5 YR	1.8		1.1
Ah ₁ O 3	0.15 Y	3.0		1.25	0.6 Y	1.5		0.9
Ah ₂ E 1	0.85 Y	3.45		1.80	0.6 Y	2.15		1.75
Ah ₁ E 1	0.4 Y	3.2		1.5	0.1 Y	2.1		1.5
Ah ₂ E 2	0.4 Y	2.85		1.3	9.95 YR	1.65		0.95
Ah ₁ E 2	0.15 Y	2.6		1.1	0.1 Y	1.7		0.9
Ah ₂ E 3	0.15 Y	3.3		1.65	9.7 YR	1.9		1.5
Ah ₁ E 3	0.2 Y	2.7		1.15	0.4 Y	1.6		0.9

- * Ah₁ - Ah₁ horizon
 PC - Pincher Creek sample
 O - Olds sample
 E - Edmonton sample
 1 - site 1
 2 - site 2
 3 - site 3
 4 - site 4

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